



# Photophysics of nanographenes: from polycyclic aromatic hydrocarbons to graphene nanoribbons

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## Abstract

Graphene quantum dots (GQDs) and nanoribbons (GNRs) are classes of nanographene molecules that exhibit highly tunable photophysical properties. There have been great strides in recent years to advance our understanding of nanographene photophysics and develop their use in light-harvesting systems, such as artificial photosynthesis. Here, we review the latest studies of GQDs and GNRs which have shed new light onto their photophysical underpinnings through computational and advanced spectroscopic techniques. We discuss how the size, symmetry, and shape of nanographenes influence their molecular orbital structures and, consequentially, their spectroscopic signatures. The scope of this review is to comprehensively lay out the general photophysics of nanographenes starting with benzene and building up to larger polycyclic aromatic hydrocarbons, GQDs, and GNRs. We also explore a collection of publications from recent years that build upon the current understanding of nanographene photophysics and their potential application in light-driven processes from display, lasing, and sensing technology to photocatalytic water splitting.

**Keywords** Graphene · Quantum dot · Nanoribbon · Polycyclic · Aromatic · Hydrocarbons · Exciton · Coherence · Diffusion · Binding energy

## Introduction

Since the first isolation of single-layer graphene in 2004, there has been an explosion of studies reporting the outstanding electronic, thermal, and mechanical properties of this two-dimensional crystal (Allen et al. 2010). However, the optical properties of single-layer graphene have remained elusive because it is a semimetal with a zero bandgap (Bodenmann and MacDonald 2007). To widen the bandgap, recent synthetic efforts have been directed toward quantum confined two-dimensional nanographenes, such as polycyclic aromatic hydrocarbons (PAH), graphene quantum dots (GQDs) and graphene nanoribbons (GNRs). Since their size is smaller than the essentially infinite exciton Bohr

radius of bulk graphene (Li and Yan 2010), these nanographenes exhibit tunable excitonic properties suitable for many optoelectronic applications. Optical properties of nanographenes can also be tuned using varied aromatic stability, as predicted by Clar's sextet rule (Clar 1983), or using molecular symmetry (Kastler et al. 2006; Dumsclaff et al. 2016) to generate a myriad of structures with electronic transitions that span the UV, Vis, and near IR regions. These properties, combined with high mobility of free charge carriers along the nanographene axes (Morozov et al. 2008; Hong et al. 2009) have enabled the utilization of nanographenes in many optoelectronic applications, such as light-emitting diodes (Wang et al. 2017, 2020; Yuan et al. 2018, 2019a, 2020; Zhao et al. 2019; Cho et al. 2020; Pramanik et al. 2020), photovoltaic devices (Qin et al. 2015; Khan and Kim 2018; Gan et al. 2019) and photocatalytic systems (Yan et al. 2018, 2020; Tsai et al. 2020).

Given the recent growth of research articles reporting optoelectronic properties of nanographenes, we provide here a comprehensive review of fundamental nanographene photophysics and photochemistry. We anticipate that this work will complement other review articles focusing on

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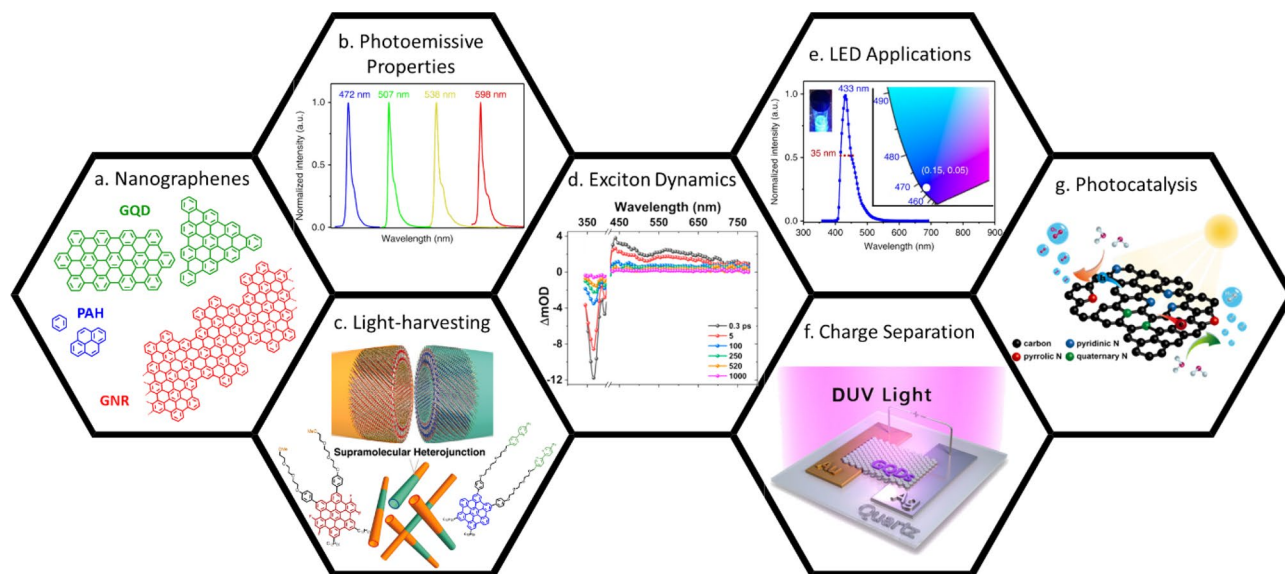
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the synthesis and electronic properties of nanographenes. Specifically, photophysical nanographene studies described here are enabled by rapidly growing developments in synthetic methodologies for bottom-up synthesis of well-defined carbon structures. Several recent reports describe these advances and illustrate the richness of possible carbon and heteroatom-containing structures that can be formed using wet-chemistry reactions such as condensations, electrocyclic reactions, oxidative dehydrogenation, and many others (Narita et al. 2015; Stepień et al. 2017; Wang et al. 2019; Yano et al. 2020). Previous reviews of electronic properties in nanographenes provide information on how molecular size, shape, edge structure, and heteroatom insertion can affect the electronic conductivity and energy gaps (i.e. HOMO–LUMO gap) in these species (Rieger and Müllen 2010; Tang et al. 2013). While some of these properties are not directly related to the photophysical studies reported here, energy gap tuning is directly related to the ability to control the frequencies at which light is absorbed. Additionally, charge carrier mobilities are important in photocatalysis, where the photoinduced electron transfer to the catalytic sites form charge carriers that need to quickly migrate away from each other. Finally, previous reviews describing

applications of nanographenes in sensing, light-emitting diodes, photodetectors, and photocatalysis provide insights into how fundamentally interesting excited-state properties of nanographenes can be applied in material science (Li et al. 2015a). This review summarizes the fundamental photophysical and photochemical behavior of nanographenes by building on the lessons learned from decades of research involving small PAH, such as benzene and pyrene. The excited-state behavior of PAH will be used as a platform for understanding how larger nanographenes behave and how their behavior affects their applications in material science.

Our review outlines the excited-state behavior of nanographenes, which are grouped into PAH, GQDs and GNRs (Fig. 1a). This classification is arbitrary and used here only to adhere to the terminology commonly used in the literature. For the purpose of this review, we define PAH as nanographenes with less than 13 fused rings. GQDs and GNRs are defined as nanographenes with more than 13 fused rings and differ from each other based on their shape (radiant GQDs vs linear GNRs). For brevity, non-planar nanocarbon materials, such as fullerenes, carbon nanotubes and other curved nanographenes are not discussed in this review, since the photophysics of these structures have been discussed by



**Fig. 1** **a** Structures of representative nanographenes reviewed here: PAH (blue), GQDs (green), and GNRs (red). **b** Emission spectra of four triangular GQDs of varying size (all samples were excited at 375 nm). Adapted from Ref (Yuan et al. 2018). **c** Structures of nanotubular heterojunctions, Block-NT1Cu/NT2, formed via self-assembly of hexabenzocoronene-based GQDs HBC 1 and HBC 2. Block-NT1Cu/NT2 was shown to undergo efficient excitation energy transfer across the supramolecular heterojunction using steady-state fluorescence experiments. Adapted from Ref. (Zhang et al. 2011) **d** Femtosecond transient absorption spectra for hexabenzocoronene (HBC) thin film showing decay of the signal with time representing the recombination of excitons. The sample was excited at 405 nm with pump intensity of

500 nJ per pulse with parallel polarization of pump and probe beams. **e** CIE color coordinates of conventional deep-blue carbon dot's (C-DB-CD's) and high-colour-purity deep-blue carbon dot's (HCP-DB-CD's) emission spectra. Adapted from Ref: (Yuan et al. 2020). **f** Schematic of deep-UV photodetector fabricated from a quartz substrate with Au (anode) and Ag (cathode) electrodes connected through light-absorbing, hydrothermally synthesized GQDs possessing high responsivity and detectivity. Adapted from Ref. (Zhang et al. 2015) **g** Proposed mechanistic scheme for photocatalytic CO<sub>2</sub> reduction by a nitrogen-doped graphene quantum dot under solar illumination. Adapted from Ref: (Tsai et al. 2020)

others (Jorio et al. 2004; Dresselhaus et al. 2007; Carlson and Krauss 2008; Miyauchi 2013; Segawa et al. 2016; Soavi et al. 2016b; Dai et al. 2018; Majewski and Stępień 2019).

We begin with the *General Photophysics* section, where fundamentals of PAH excited states are described. Using simple Hückel theory, we provide a description of transitions commonly observed in the electronic spectra of PAH and the effects of symmetry and heteroatom substitution on the transition energies and oscillator strengths. This section also describes the effect of intermolecular  $\pi$ -interactions, which are important modulators of nanographene photophysics, particularly as the number of phenyl rings becomes large. The second section, titled *Energy Gap Tuning*, describes various methods by which electronic transitions in nanographenes are tuned by varying molecular size and shape (for example, Fig. 1b), or by insertion of heteroatoms. The third section, titled *Energy and Electron Transfer*, describes the efficiency of coherent and incoherent energy transport in nanographenes and their  $\pi$ -stacked assemblies (Fig. 1c,d). Furthermore, this section describes photoinduced electron transfer processes in nanographenes that contain transition metal centers. The *Applications* section provides selected examples of optoelectronic materials made of nanographenes, such as light-emitting diodes (LEDs, Fig. 1e), lasing media, photodetectors (Fig. 1f) and photocatalysis (Fig. 1g). Lastly, the *Future Directions* section provides the outlook of this field and the challenges that the nanographene community faces moving forward.

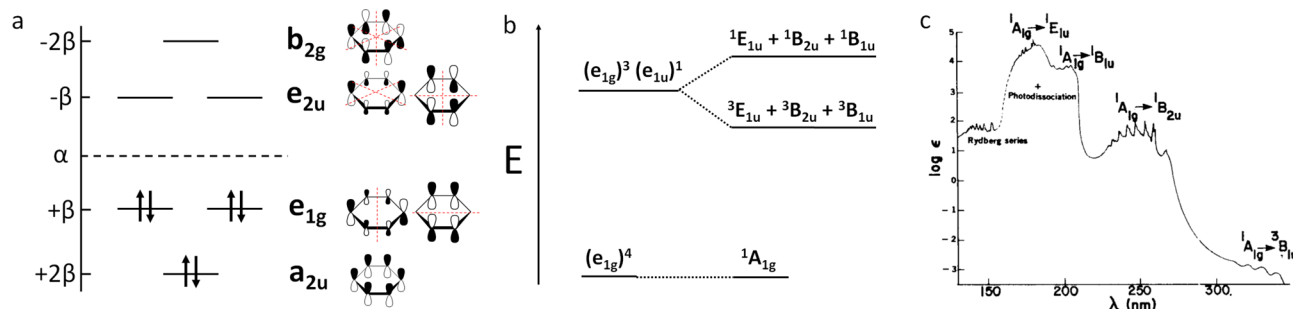
## General photophysics

This section outlines the fundamental optical properties of nanographenes using simple PAH as representative examples. Since PAH are predominantly made of  $sp^2$  carbon atoms, their UV/Vis absorption signatures are often attributed to  $\pi$ - $\pi^*$  electronic transitions. When heteroatoms with lone pairs (such as N) are present in the aromatic framework, additional  $n$ - $\pi^*$  transitions are also possible. However, these

transitions are usually not relevant for the photophysics of nanographenes because they are higher in energy and lower in intensity than the  $\pi$ - $\pi^*$  transitions. The energies of  $\pi$ - $\pi^*$  transitions vary with the size and shape of the nanographene molecule, as we will discuss in the next section. Here, we explore how the intensities of  $\pi$ - $\pi^*$  transitions are affected by the molecular structure. Predictions from group theory rely on the selection rules that require a nonzero transition dipole moment for allowed transitions which is achieved only if the direct product:

$$\Gamma(\psi_e) \times \Gamma(\hat{\mu}_e) \times \Gamma(\psi_g) \quad (1)$$

contains the totally symmetric irreducible representation of the point group of the molecule (Harris and Bertolucci 1989). The first term,  $\Gamma(\psi_e)$ , is the irreducible representation for molecule in its ground state. Since most PAH have all electrons paired up in the ground state,  $\Gamma(\psi_e)$  will be the totally symmetric irreducible representation of the point group of that PAH (for example, benzene belongs to  $D_{6h}$  point group, so  $\Gamma(\psi_e)$  for benzene is  $A_{1g}$ ). The second term,  $\Gamma(\hat{\mu}_e)$ , is the irreducible representation for the dipole moment operator. Since the dipole moment operator transforms the  $x$ ,  $y$ , and  $z$  coordinates of the system,  $\Gamma(\hat{\mu}_e)$  of the molecule can be found from the character table (in the case of  $D_{6h}$  group,  $A_{2u}$  and  $E_{1u}$  are the irreducible representations for  $\Gamma(\hat{\mu}_e)$ ). The third term,  $\Gamma(\psi_g)$ , is the irreducible representation for the PAH in its excited state. For a totally symmetric ground state,  $\Gamma(\psi_g)$  must be the same as one of the  $\Gamma(\hat{\mu}_e)$  representations for the triple product (1) to contain a totally symmetric representation. In the case of benzene,  $\Gamma(\psi_g)$  states can be predicted from the analysis of molecular orbitals (MOs) obtained using a simple Hückel model (Fig. 2a, b). Absorption of an ultraviolet photon by a single molecule of benzene can promote it from the ground state ( $S_0$ ) to an electronically excited state ( $S_n$ ). The HOMO and LUMO of benzene each consist of a pair of degenerate MOs where electron correlation interactions result in three  $S_0$   $S_n$  transitions which are observable as  $\alpha$ -,  $\beta$ -, and  $\gamma$ -bands in the



**Fig. 2** **a** Molecular orbital energy diagram of benzene with bonding/antibonding structures at the side. **b** molecular orbital energy splitting in benzene. **c** UV-vis absorption spectrum of benzene (Harris and Bertolucci 1989)

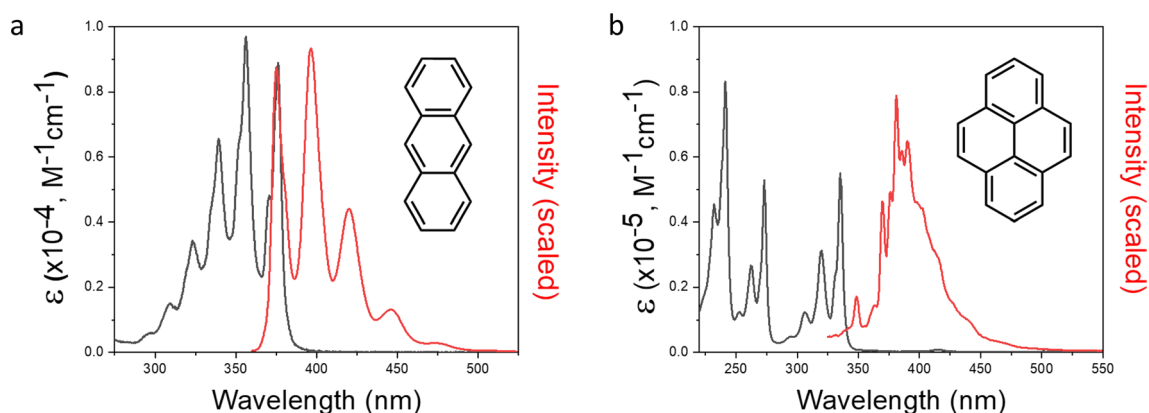
UV/Vis absorption spectrum (Rieger and Müllen 2010). Del Bene and Jaffé investigated the impact of symmetry-breaking in 1968, setting the stage for the role of symmetry and non-bonding ( $n$ ) orbitals in mono-sextet nanocarbons (Bene and Jaffé 1968). Analysis of the lowest three excited states of benzene indicates that one transition will be allowed ( $^1A_{1g} \rightarrow ^1E_{1u}$ ) while two will be orbitally forbidden ( $^1A_{1g} \rightarrow ^1B_{2u}$  and  $^1A_{1g} \rightarrow ^1B_{1u}$ ). This analysis predicts the experimentally observed absorption bands of benzene well (Fig. 2c). In general, the orbitally allowed transitions exhibit extinction coefficients in the  $10^3$ – $10^5$   $M^{-1} \text{ cm}^{-1}$  range, while the orbitally forbidden transitions are in the  $10^0$ – $10^3$   $M^{-1} \text{ cm}^{-1}$  range (Turro et al. 2009). Here, we consider the relationship between the symmetry of benzene and its photophysical properties, namely, its energy gap (we discuss nanographene energy gaps in more detail in the next section). The allowed  $^1A_{1g} \rightarrow ^1E_{1u}$  transition in benzene occurs at an energy of 6.9 eV ( $\sim 180$  nm) while the longer wavelength  $^1A_{1g} \rightarrow ^1B_{2u}$  and  $^1A_{1g} \rightarrow ^1B_{1u}$  transitions are symmetry forbidden. The addition of a heteroatom nitrogen to the aromatic ring (pyridine) breaks the  $D_{6h}$  symmetry of benzene and increases the intensity of the forbidden transitions. Furthermore, pyridine and the diazines exhibit  $n\text{--}\pi^*$  transitions in the 3.3–4.3 eV range due to the interaction of the nitrogen lone pairs with the  $\pi^*$  acceptor MO.

As the shape of the PAH changes, the intensity of the low-energy transition changes based on the triple product (1) discussed above. For example, anthracene and pyrene (both with  $D_{2h}$  symmetry) exhibit different intensities of their lowest energy electronic transitions due to different  $\Gamma(\psi_e)$  values for the first excited state (allowed for anthracene and forbidden for pyrene, Fig. 3) (Turro et al. 2009). Differences in oscillator strengths of the lowest excited states also affect the fluorescence lifetimes, as predicted by relationships between the Einstein coefficients for absorption and emission: electronic transition that are allowed have intense

absorption bands, but small fluorescence lifetimes and vice versa. This effect can be clearly observed in Fig. 3 showing the absorption and emission spectra of anthracene ( $\epsilon \sim 10^5$   $M^{-1} \text{ cm}^{-1}$ ;  $\tau \sim 10$  ns) and pyrene ( $\epsilon \sim 10^2$   $M^{-1} \text{ cm}^{-1}$ ;  $\tau \sim 1$   $\mu$ s).

Spin–orbit coupling in PAH is generally weak, which is consistent with the small atomic numbers of their constituent carbon and hydrogen atoms. For this reason, intersystem crossing from singlet to triplet excited states in PAH generally occurs with rates of  $10^6$ – $10^8$   $s^{-1}$  (Turro et al. 2009). These values are comparable with the rate of fluorescence in PAH, so the conversion to triplet states is often observed from lowest-energy singlet excited states. Interestingly, intersystem crossing can also be observed from higher singlet excited states  $S_2$ ,  $S_3$ , etc. as the nanographene size increases (Mueller et al. 2010). This behavior is associated with the so-called energy gap law derived from perturbation theory, which states that the mixing of singlet and triplet states due to spin–orbit coupling is inversely proportional to the difference in their energies,  $\Delta E_{ST} = E_S - E_T$ . For small PAH, the  $\Delta E_{ST}$  values are usually large (up to 1 eV) which results in slow rates for triplet formation. The  $\Delta E_{ST}$  value is inversely proportional to the size of the nanographene and the gap becomes as small as 0.175 eV for a GQD with diameter of 2.5 nm, resulting in triplet  $T_1$  state generation even directly from higher singlet  $S_2$  and  $S_3$  states (Mueller et al. 2010).

Intermolecular interactions between nanographene molecules can drastically change their photophysical behavior. Specifically, it is well known that an increase in the nanographene surface area leads to  $\pi$ – $\pi$  interactions between them and lower solubility (Watson et al. 2001). The origin of these  $\pi$ – $\pi$  interactions was initially ascribed to the quadrupole moment associated with the  $\pi$ -electron density, but recent theoretical studies point to the dispersion forces as the leading factor for  $\pi$ – $\pi$  interactions in large nanographenes (Grimme 2008; Martinez and Iverson 2012). Once



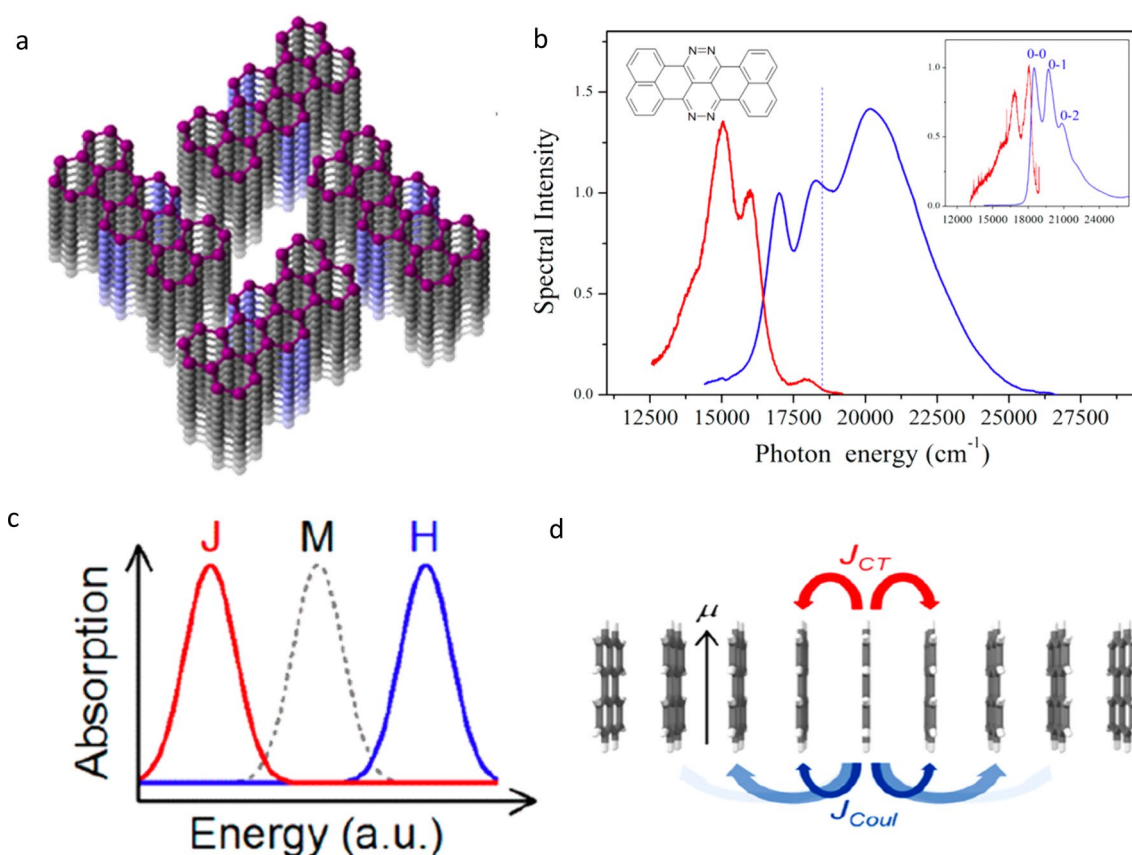
**Fig. 3** Absorption (black) and emission (red) spectra of **a** anthracene ( $\tau = 5.3 \pm 0.1$  ns,  $\Phi = 0.36$ ) and **b** pyrene ( $\tau = 338 \pm 9$  ns,  $\Phi = 0.32$ ) (Berman 1971; Nakajima 1973; Boens et al. 2007)



aggregated, the PAH chromophores no longer behave as isolated systems, but start developing new excitonic features. This effect is exemplified in the UV/Vis absorption and emission spectra of tetraazaterrylene (TAT) in dilute solution and thin crystalline film, where TAT forms  $\pi$ -stacked nanopillar structures (Fig. 4a, b). While TAT in dilute solution exhibits narrow bands with clear vibronic progression, the bands of the thin film are much broader, and the peaks appear at different frequencies (Yamagata et al. 2014).

To better understand the excited state photophysics of nanographene chromophores, we must consider the concept of the exciton, a quasiparticle composed of an electron–hole pair. Excitons are defined as electronic excited states that do not reside on a single chromophore, but are expressed as a linear combination of individual chromophore eigenstates. Since PAH-based  $\pi$ -aggregates exhibit low dielectric constants, their excitons are of the Frenkel type where photo-generated electron and hole reside on the same molecule (no charge-transfer states) (Scholes and Rumbles 2006; Cudazzo et al. 2015; Ilic et al. 2017; Tries

et al. 2020). The shifts in the absorption and emission spectra of  $\pi$ -aggregates can be predicted using perturbation theory, where the “perturbative” interaction between the chromophores is expressed as a combination of the long-range Coulombic interactions ( $J_{\text{coul}}$ ) and short-range exchange interactions ( $J_{\text{CT}}$ ) (Hestand and Spano 2017). Long-range coupling ( $J_{\text{coul}}$ ) is associated with the interactions between transition dipole moments of individual chromophores and has been successfully used to describe the red- and blue-shifts in the electronic transition energies of J and H aggregates of many organic chromophores (Fig. 4c). The short-range exchange coupling ( $J_{\text{CT}}$ ) is associated with Dexter-type electron transfer between individual chromophores and can be modeled as a charge-transfer, state-mediated process (Fig. 4d). The additive contributions of  $J_{\text{coul}}$  and  $J_{\text{CT}}$  terms are needed to describe the complicated spectral changes associated with  $\pi$ -stacked PAH chromophores and this model has been shown to successfully reproduce the experimental spectra of TAT (Yamagata et al. 2014).



**Fig. 4** **a** Crystal structure of 7,8,15,16-tetraazaterrylene (TAT) aggregates, **b** Absorption (blue) and emission (red) spectra of TAT (inset; spectra of 100 nM solution of TAT in chloroform), **c** Ideal absorption

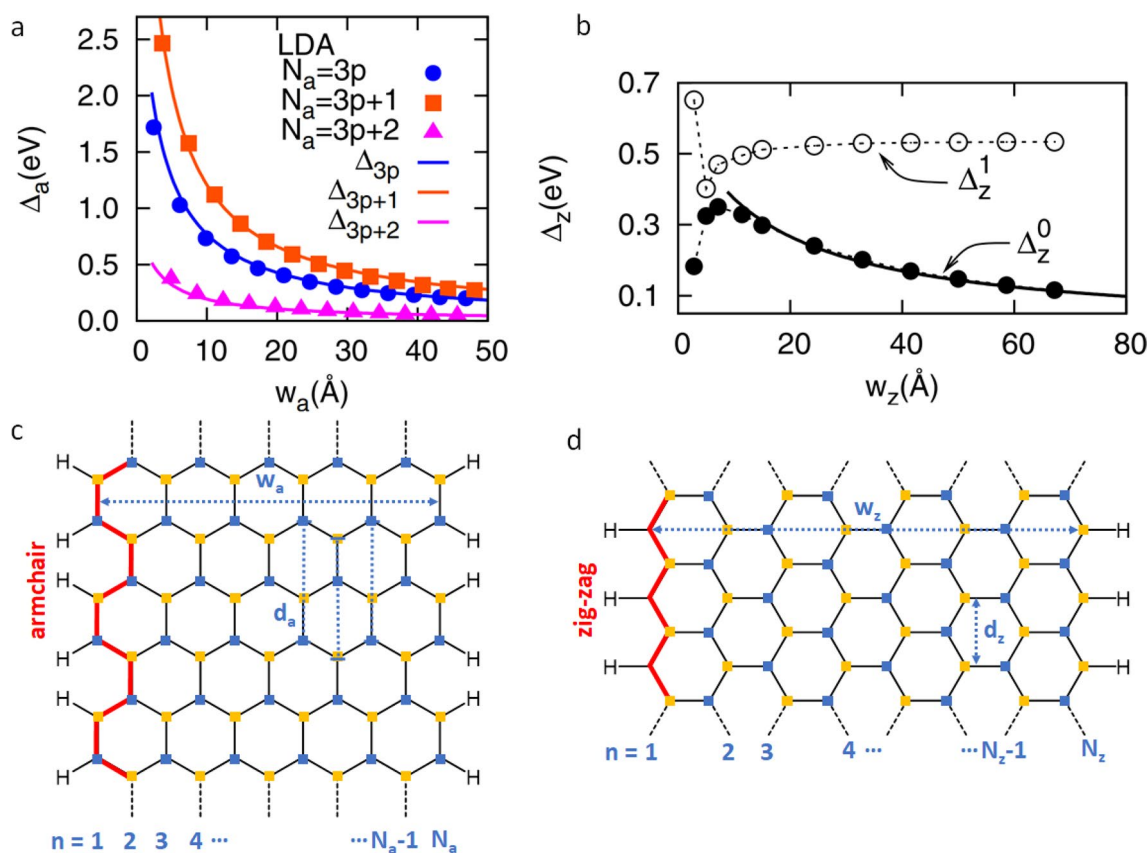
spectra for J- and H-aggregates, **d** Model of short-range, charge-transfer-mediated interactions,  $J_{\text{CT}}$ , and long-range Coulomb interactions,  $J_{\text{coul}}$  (Yamagata et al. 2014; Hestand and Spano 2017)

## Energy gap tuning

When other structural parameters (edge-structure, symmetry, chemical functionalization, etc.) are held constant, there exists an inversely proportional relationship between the size of a nanographene and the magnitude of its energy gap. For example, theoretical analysis of zig-zag and armchair GQDs has shown that the energy gap in GQDs falls off with  $1/N$ , where  $N$  is the number of hexagonal units along the edge of the GQD (Zhang et al. 2008). Similar behavior was observed for GNRs, where the gap was found to fall off  $1/w$ , where  $w$  is the width of the nanoribbon (Fig. 5a, b) (Son et al. 2006). However, the exact relationship between GNR width and energy gap is a bit more complicated than this. Armchair-GNRs can be grouped into different subfamilies with  $N_a = 3p$ ,  $3p + 1$ , and  $3p + 2$ , where  $N_a$  is the number of dimer lines ( $d_a$ ) across the width of the GNR and  $p$  is an integer (Fig. 5c). The energy gaps of these families of GNRs follow the trend  $3p + 2 < 3p < 3p + 1$  (Son et al. 2006). Regarding

zig-zag GNRs, the relationship between energy gap and ribbon width appears to follow the simple inversely proportional relationship just described (Fig. 5d).

Recent developments in the bottom-up synthesis of nanographenes (Huang et al. 2018; Zhao et al. 2018; Singh et al. 2020b) have enabled the synthesis and spectroscopic investigation of well-defined molecules and the results of these experiments generally confirm the theoretical predictions. It has been demonstrated that the energy gaps of fully benzenoid PAH decrease from 3.9 eV in triphenylene (a 4 fused-ring PAH) to 2.2 eV for a larger, 15-ring GQD (Rieger and Müllen 2010). This relationship has been demonstrated for a wide variety of PAH and GQDs that take on many different morphologies. For example, triangular-GQDs (T-GQDs) exhibit a progressive redshift in absorbance and emission peaks with increasing size (Yuan et al. 2018). GQDs of other shapes, such as hexa-*peri*-hexabenzocoronene (HBC) derivatives, have the same inversely proportional relationship between their sizes and optical gaps (Zhang et al. 2015). Systematic energy gap engineering in GQDs via extension of the conjugated  $\pi$ -system (by



**Fig. 5** **a** Energy gap as a function of GNR width where  $N_a$  is the number of dimer lines ( $d_a$ ) across the ribbon width and  $p$  is an integer. **b** Bandgap ( $\Delta_z^0$ ) and energy splitting ( $\Delta_z^1$ ) of zig-zag GNRs as a function of ribbon width. **c** Representative structure of an armchair GNR where  $w_a$  is the width and  $d_a$  is the 1D unit cell distance. Char-

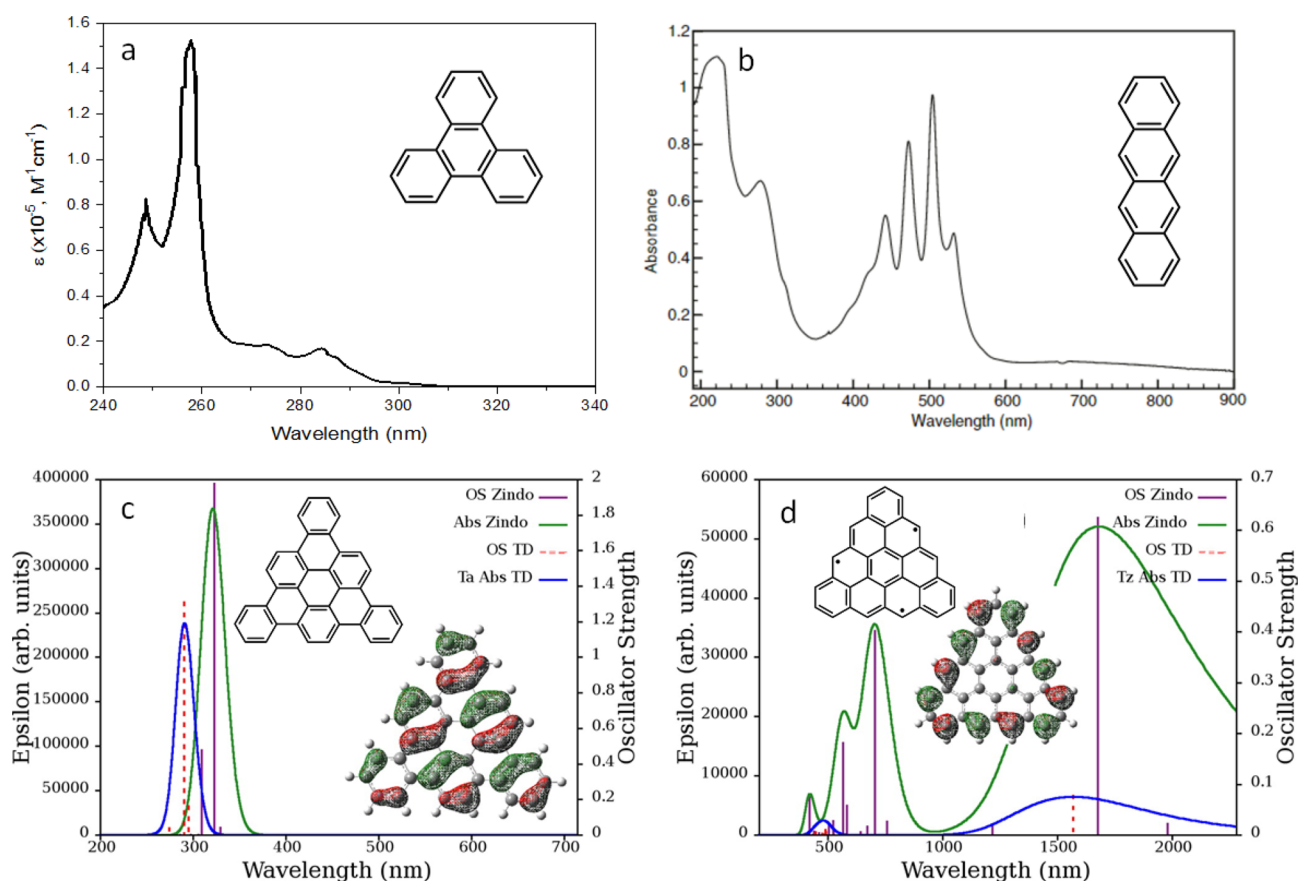
acteristic armchair edge is highlighted in red. **d** Representative structure of a zig-zag GNR where  $w_z$  is the width and  $d_z$  is the 1D unit cell distance. Characteristic zig-zag edge is highlighted in red (Son et al. 2006)

solvothermal condensation with aromatic ligands) has been shown to stabilize the  $\pi^*$  acceptor MO energy resulting in a narrowing of the energy gap by 0.52 eV (Yan et al. 2018). Energy gap tuning in GNRs is accomplished using similar strategies. Narita and coworkers demonstrated the length-dependent quantum confinement effect in GNRs in a 2013 study which shows a red-shift absorption band as the nanographene increases in length from dimer to trimer to nanoribbon (Narita et al. 2014).

Nanographene edges play a significant role in the energy gap as well (Yamijala et al. 2015; Ivanov et al. 2017; Dumsclaff et al. 2020). The size dependence presented in Fig. 5 shows that the energy gap in GQDs falls off more drastically with  $N$  if the edges are zig-zag. Similarly, zig-zag GNRs exhibit smaller gaps than armchair GNRs of similar size. This behavior can be readily described using the simple and chemically intuitive Clar's sextet rule (Solà 2013), which states that the stability of a given PAH is proportional to the number of benzene-like  $\pi$ -sextet moieties that it contains. For example, triphenylene is much more stable than tetracene (Fig. 6a, b). Similarly, larger nanographenes with

armchair edges have more  $\pi$ -sextets than those with zig-zag edges (as exemplified for triangular GQDs in Fig. 6c, d). Additionally, zig-zag PAH contain more nodes than armchair PAH. The presence of these nodes destabilize the HOMO level which narrows the energy gap (Yamijala et al. 2015). The increased stability of PAH is associated with large energy gaps, explaining the trends observed in Fig. 5 and the UV/Vis absorption spectra in Fig. 6 (Yamijala et al. 2015).

Clar's sextet rule can also be used to explain the dependence of the energy gap on the shape of the nanographene (Rieger and Müllen 2010). For example, triphenylene and tetracene are both 4-ring (18 carbon atoms in total) PAH. However, triphenylene contains three Clar's sextets while tetracene contains only one (see Fig. 6a, b), which results in tetracene exhibiting lower energy absorption than triphenylene as well as higher reactivity. Nanographene symmetry can also be used to tune the energy gaps. For example, Müllen and co-workers investigated a series of HBC-derivatives synthesized to have different symmetries ( $D_{6h}$ ,  $C_{2v}$ ,  $D_{2h}$ , and  $D_{3h}$ ) (Kastler et al. 2006; Dumsclaff et al. 2016).



**Fig. 6** **a** Absorption spectrum of triphenylene with structure in inset. **b** Absorption spectrum of tetracene (film deposited on a  $MgF_2$  disk) with structure in inset. **c** Calculated absorption spectrum of an armchair T-GQD, inset shows Clar's sextet structure (top) and calculated

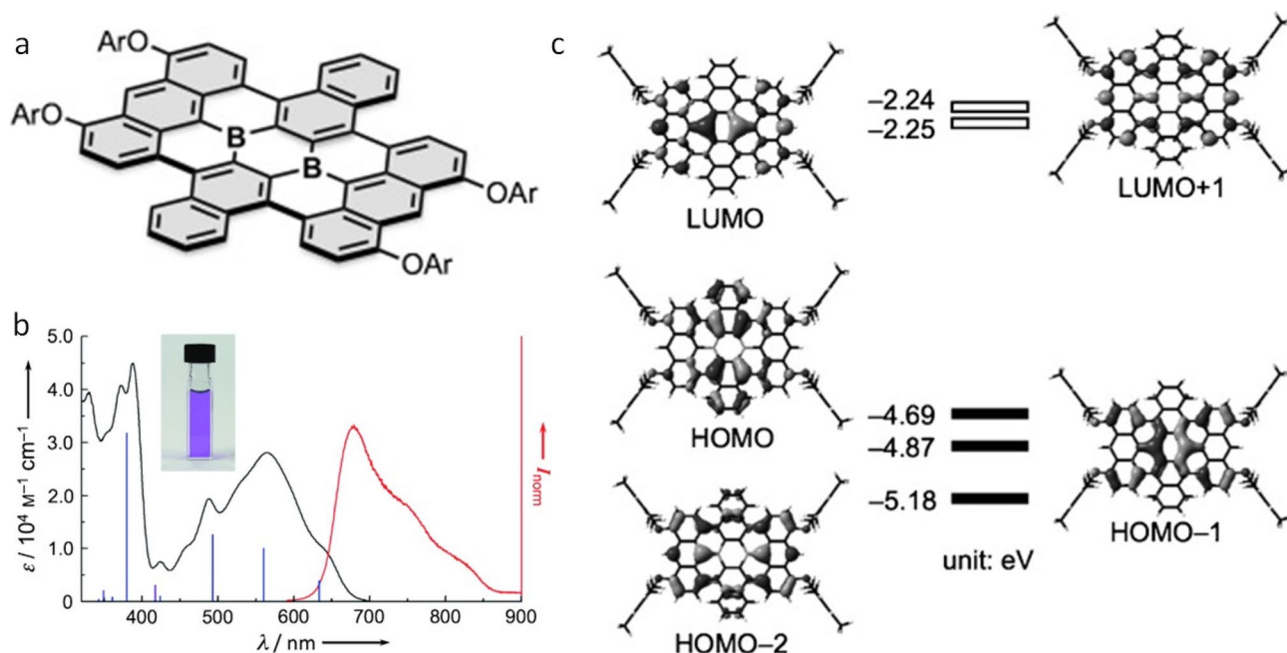
HOMO isosurface (bottom). **d** Calculated absorption spectrum of a zig-zag T-GQD, inset shows Clar's sextet structure (top) and calculated HOMO isosurface (bottom) (Talrose et al. 2020; Bryson et al. 2011; Yamijala et al. 2015)

The authors found that higher symmetry GQDs (such as  $D_{6h}$ ) exhibit narrow UV/Vis bands with few transitions and broader photoluminescence (PL) spectra compared to lower symmetry PAH (such as  $C_{2v}$ ). Reduction in symmetry leads to more allowed transitions and, consequently, broader and less featured UV/Vis spectra and similar shape-dependent behavior was observed in other nanographenes (Rieger and Müllen 2010; Stępień et al. 2017).

Edge functionalization is another strategy for tuning the energy gaps of GQDs due to the charge transfer effects of electron donating and withdrawing groups (Bao et al. 2011; Wang et al. 2016; Hai et al. 2018; Yuan et al. 2018). Yun Li et al. carried out a computational study on the electronic and optical properties of GQDs edge-functionalized with  $-NH_2$ ,  $-OH$ ,  $-F$ ,  $-CHO$ ,  $-COCH_3$ , and  $-COOH$  groups (Li et al. 2015b). Density functional theory (DFT) calculations of C=O functionalized GQDs predict the lowering of HOMO and LUMO energy levels due to the  $\pi$ -electrons in C=O that can extend the  $\pi$ -electron system in the GQD moiety. Amino groups may also tune the optical properties of GQDs, but their influence on the energy gap is much weaker due to the cancellation of the frontier orbital hybridization effect by larger charge transfer effects. Yuan et al. demonstrated the importance of amination by comparing the optical properties of aminated and non-aminated GQDs where the aminated analogs exhibited a larger emission full-width at half-maximum (FWHM) of 62 nm, possessed a bandgap of 2.96 eV, and quantum yield (QY) of 70% (Yuan et al. 2020). The promising results of aminated GQDs is

attributed to the reduced defects in the GQD structure which significantly reduces non-radiative pathways. It should also be noted that amination reduces the symmetry of GQDs which manifests in the red shifted calculated absorption and emission spectra (Wang et al. 2016). Furthermore, tailoring electron-donating groups to the peripheries of GQDs results in the creation of non-bonding ( $n$ ) orbitals that lay higher in energy than the  $\pi$  donor MO of the GQD, but lower in energy than the  $\pi^*$  acceptor MO, which has narrowed the gap of coal-derived GQDs from 2.40 eV to 1.94 eV (Yan et al. 2020). Conversely, electron withdrawing groups can reduce the energy gap in GQDs as demonstrated by the 100 nm emission wavelength red shifting of chlorine atom (Cl) functionalized GQDs (Zhao et al. 2018).

Energy gap tuning has also been demonstrated by introducing heteroatoms to the  $sp^2$  carbon framework of GQDs and GNRs, such as B, N and O atoms (Dou et al. 2012; Cloke et al. 2015; Kawai et al. 2015, 2018; Tsai et al. 2020). For example, the introduction of boron atoms into GQDs results in significant energy lowering of the absorption and emission bands (Fig. 7a, b) (Dou et al. 2012). The corresponding DFT calculations show that the observed lowering of electronic transition energies is associated with the significant contribution of boron 2p orbitals to the frontier orbitals of the GQD (Fig. 7c). Similarly, the optical gap of GQDs have been controllably altered from 2.31 eV to lower energies such as: 2.18 eV for N-doped, 2.12 eV for S-doped, and 2.04 eV for N,S-doped GQDs (Yan et al. 2020). The location of nitrogen heteroatoms in the GQD flake (pyridinic



**Fig. 7** **a** Structure of a boron heteroatom-containing PAH (B-PAH). **b** Measured UV-vis absorption (black) and emission (red) spectra of B-PAH **c** Calculated MO energies of B-PAH (Dou et al. 2012)



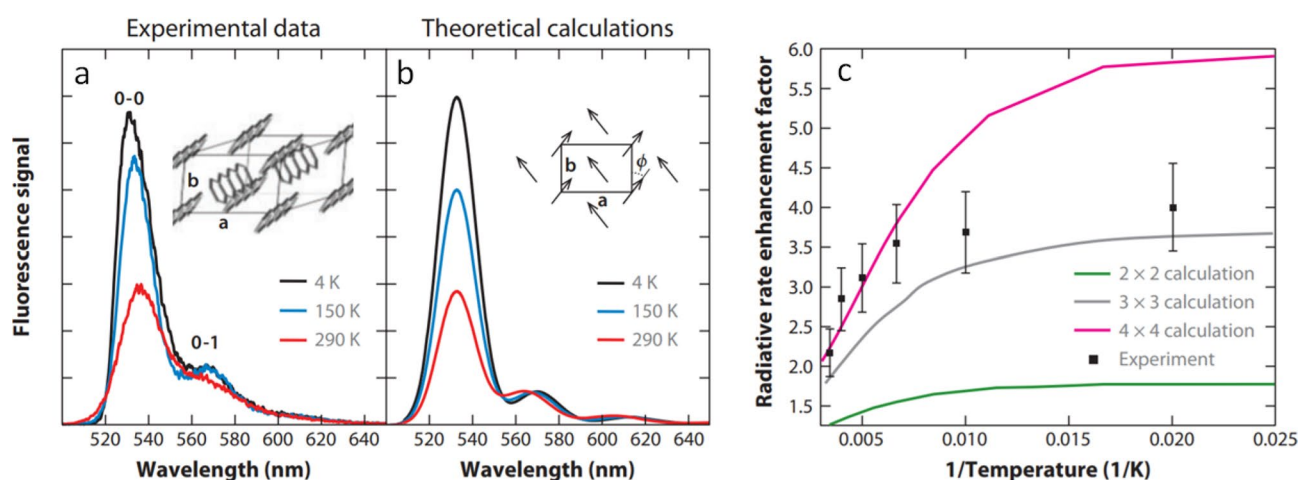
edge, pyridinic center, pyrrolic, graphitic, or amine) also plays a role in the energy gap where it has been reported that amines tend to red-shift GQD emission whereas pyridinic nitrogen atoms tend to blue-shift it (Calabro et al. 2019; Tsai et al. 2020).

## Energy and electron transfer

Electronic excitation energy transport in nanographenes has been explored for two types of systems. One involves intramolecular excitation transfer along the covalently linked framework of a single nanographene (such as GNR) and another involves intermolecular assembly of nanographenes (such as  $\pi$ -stacked GQDs). These covalent and  $\pi$ -stacked architectures are multi-chromophore systems: GNRs are defined as covalently linked arrays of chromophores, where each chromophore is spatially located on a single monomeric unit, while GQD assemblies are an array of GQD chromophores held together by van der Waals interactions. Electronic excitation transport between these chromophores can be either coherent or incoherent, depending on the degree of electronic coupling between the chromophores. If the coupling is strong, excitonic states are formed, where the coherent superposition of resonating excited states allows for energy transfer within the exciton size (Olaya-Castro and Scholes 2011). Probability amplitudes on the donor and acceptor sites of such excitonic states describe coherent energy transfer. Unfortunately, exciton coherence lengths are generally small in organic chromophore assemblies at room temperature, due to the random vibrations induced from the environment that lead to exciton decoherence and reduced role of coherent energy transport in excitonic materials. The

energy transfer between weakly coupled chromophores is described by an incoherent hopping (Förster type) mechanism, in which the excitation is localized on one chromophore unit and is transferred to another unit via the “inductive resonance” mechanism that does not require the orbital overlap between donor and acceptor sites. If the orbital overlap between the chromophores exists, the energy transport can also occur via Dexter-type mechanism, in which the excitation is transferred by coupled electron and hole transfers between the donor and acceptor chromophores. Incoherent energy transfer processes are dominant in these systems. Recent studies that report coherent and incoherent energy transport in nanographenes are discussed below.

Only a handful of studies reporting exciton coherence lengths (or exciton size; the number of chromophores over which the exciton is delocalized) in nanographenes can be found in the literature. In some cases the estimate of exciton size can be obtained from steady-state emission spectra (Spano and Yamagata 2011) by investigating the relative intensities of the 0–0 and 0–1 vibronic bands of the emission spectra. The idea behind this treatment is that at  $T=0$  K, the  $I^{0-0}$  is directly proportional to exciton size, while the intensity of the 0–1 vibronic progression is relatively insensitive to exciton size. This effect can be observed in the emission spectra of tetracene crystals shown in Fig. 8 (Lim et al. 2004). As the temperature increases, the  $I^{0-0}/I^{0-1}$  ratio decreases, as the exciton size becomes smaller due to thermally induced disorder and loss of degeneracy among the chromophore eigenstates. The modeling of experimental emission spectra provided a low-temperature exciton size estimate of  $\sim 9$  molecular units in tetracene crystals. In a study by Moran and co-workers, exciton size in tetracene and rubrene crystals was determined using low-temperature



**Fig. 8** **a** Temperature-dependent emission spectra of tetracene integrated over the first 200 ps (left) and simulated emission lineshapes of tetracene at different temperatures with fixed exciton size of 9 tetracene molecules (right). Growth of 0–0 peak at lower temperatures

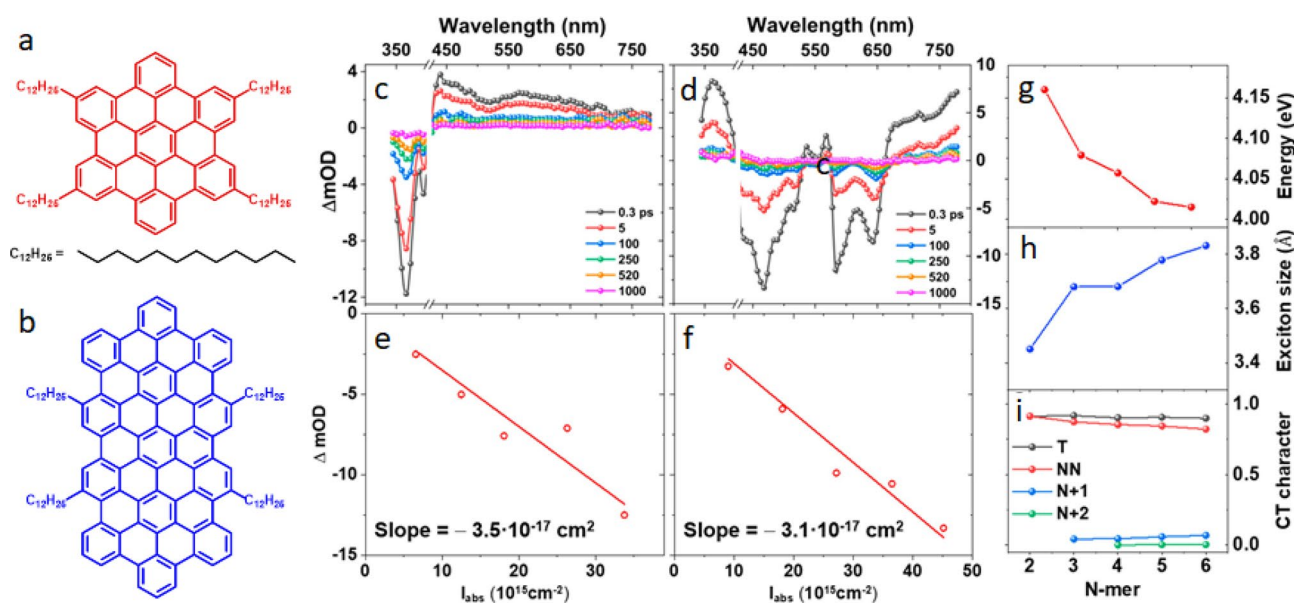
indicates an increase in singlet exciton coherence length. **b** Radiative rate enhancement as a function of temperature, measured by the amplitude of the initial fluorescence signal (Lim et al. 2004)

linear absorption spectroscopy and model calculations. The calculations showed concentration of the oscillator strength on the lowest energy transition which is a well-known signature of exciton delocalization. The exciton size was found to be  $\sim 18$  molecular units for tetracene and rubrene crystals at 200 and 78 K, respectively (West et al. 2010). In a subsequent study, Moran and coworkers determined exciton size of  $\sim 16$  molecular units in perylene crystals at 78 K using low temperature linear absorption spectroscopy and model calculations (West et al. 2011). While studies listed above investigate PAH crystals, recent studies have explored exciton coherence lengths for nanographenes and their 3D assemblies. For example, a recent study investigated exciton size in two topologically different pyrene-containing Zr-based metal–organic frameworks (MOFs) (Yu et al. 2018). In this work, exciton coherence lengths were evaluated computationally, using transition density matrices derived from time-dependent DFT. The results indicate that the excitons are delocalized over four pyrene chromophores in these systems and that the delocalization depends on the interchromophore separation in MOFs with different morphologies.

Our group recently explored 1D  $\pi$ -stacked assemblies of GQDs using transient absorption spectroscopy and DFT calculations (Fig. 9) (Singh et al. 2020b). Experimental determination of exciton size utilizes the fact that the ground-state bleach in the transient absorption signal directly reports the number and size of excitons formed by the pump beam. By

measuring the bleach signal at early times after the excitation pulse as a function of pump fluence, the exciton size in two different GQD assemblies were evaluated to be 1–2 monomer units (Fig. 9a, b). Our result was consistent with the exciton sizes calculated using the one-particle transition density formalism, where exciton size of 2 molecular units were obtained. Our results indicate very small exciton delocalization on one-dimensional aggregates. Even if the exciton size is large at the Frank–Condon point, the decoherence is generally fast and excitons generally “self-trap” on picosecond timescales (Sung et al. 2015; Kaufmann et al. 2018), providing further evidence that the coherent energy transport in these systems is not significant. While exciton size of GNRs has been explored much less, studies comparing the absorption spectra of oligomers with varying length indicate that the excitons delocalize over no more than four monomer units (Huang et al. 2018).

Incoherent energy transport (exciton diffusion length) in chromophore assemblies can be measured using various techniques such as exciton–exciton annihilation, quenching techniques and Förster resonance energy transfer (FRET) and each technique have their own advantages and disadvantages (Lin et al. 2014). Steady-state and time-resolved surface quenching techniques require steady-state or time-resolved PL measurements to determine exciton quenching in bilayers of chromophore and quencher such as  $C_{60}$  fullerene. The exciton diffusion length is estimated from the PL



**Fig. 9** Structures of alkylated **a** HBC and **b** CQD. Transient absorption spectra for **c** HBC and **d** CQD thin films in poly(methyl methacrylate) matrix. Samples were excited at  $\lambda_{exc}=405$  nm, and pump intensity was at 500 nJ per pulse with parallel pump and probe beam polarization. Circles represent  $\Delta A_{ani}(t=0)$  values obtained by probing at 367 and 467 nm [for HBC **e** and CQD **f**, respectively] as a

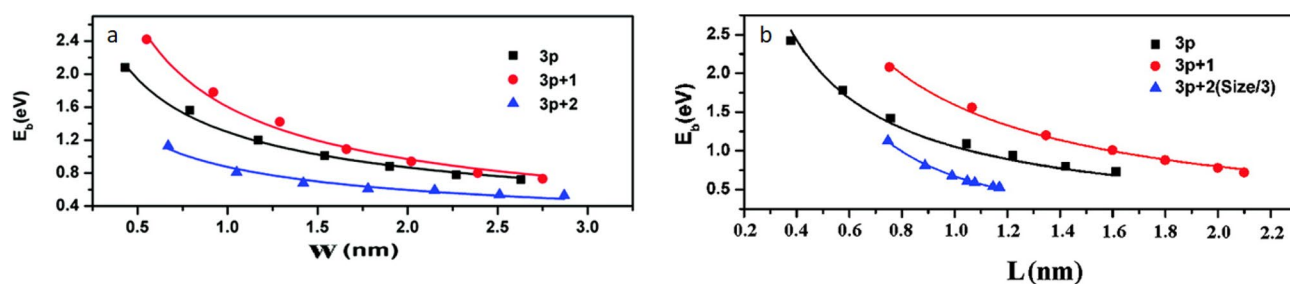
function of the absorbed pump intensity,  $I_{abs}$ . Solid lines present the fitting model. **g–i** Results from the DFT calculations on the exciton size in oligomers of the HBC model: dependence of the **g** lowest charge-transfer exciton energy, **h** size, and **i** charge-transfer character on the oligomer size  $N$  ( $T$ =total,  $NN$ =nearest neighbor,  $N+1$ =neighbor + 1, and  $N+2$ =neighbor + 2) (Singh et al. 2020b)

measurements of the chromophore layer of different thickness with and without quencher layer. Bulk quenching with Monte Carlo simulations is another technique to determine exciton diffusion parameters. Here, the chromophore with increasing concentrations of the quencher is blended and the PL lifetimes are added to the Monte Carlo simulation which provides exciton diffusion parameters. The exciton diffusion coefficients can also be determined by FRET from the spectral overlap between absorption and emission spectra of the chromophores. The exciton-exciton annihilation technique operates on the principle that at high excitation densities, two excitons can interact and annihilate with each other within their lifetime. A loss in the rate of exciton decay is observed as a function of excitation intensity and diffusivity of the excitons which can be modeled to extract exciton diffusion parameters. The article by Nguyen and coworkers (Lin et al. 2014) studies the exciton diffusion length in organic semiconductors by six different experimental techniques and a very good agreement was found. Also, semi-crystalline materials gave higher exciton diffusion coefficients when measured using exciton-exciton annihilation. One-dimensional  $\pi$ -assemblies of PAH, such as perylene bisimide stacks, have been studied extensively and an exciton diffusion length of up to 96 nm was observed using the exciton-exciton annihilation method (Marciniak et al. 2011). Our group has also explored exciton diffusion parameters for two GQD assemblies using exciton-exciton annihilation approach and diffusion length of 16 and 3 nm were found, respectively (Fig. 9). Here we observed two types of excitons: mobile and immobile, where the immobile excitons were formed due to trapping of the mobile excitons, likely caused by torsional motion of the molecules in the aggregate structure (Singh et al. 2020b).

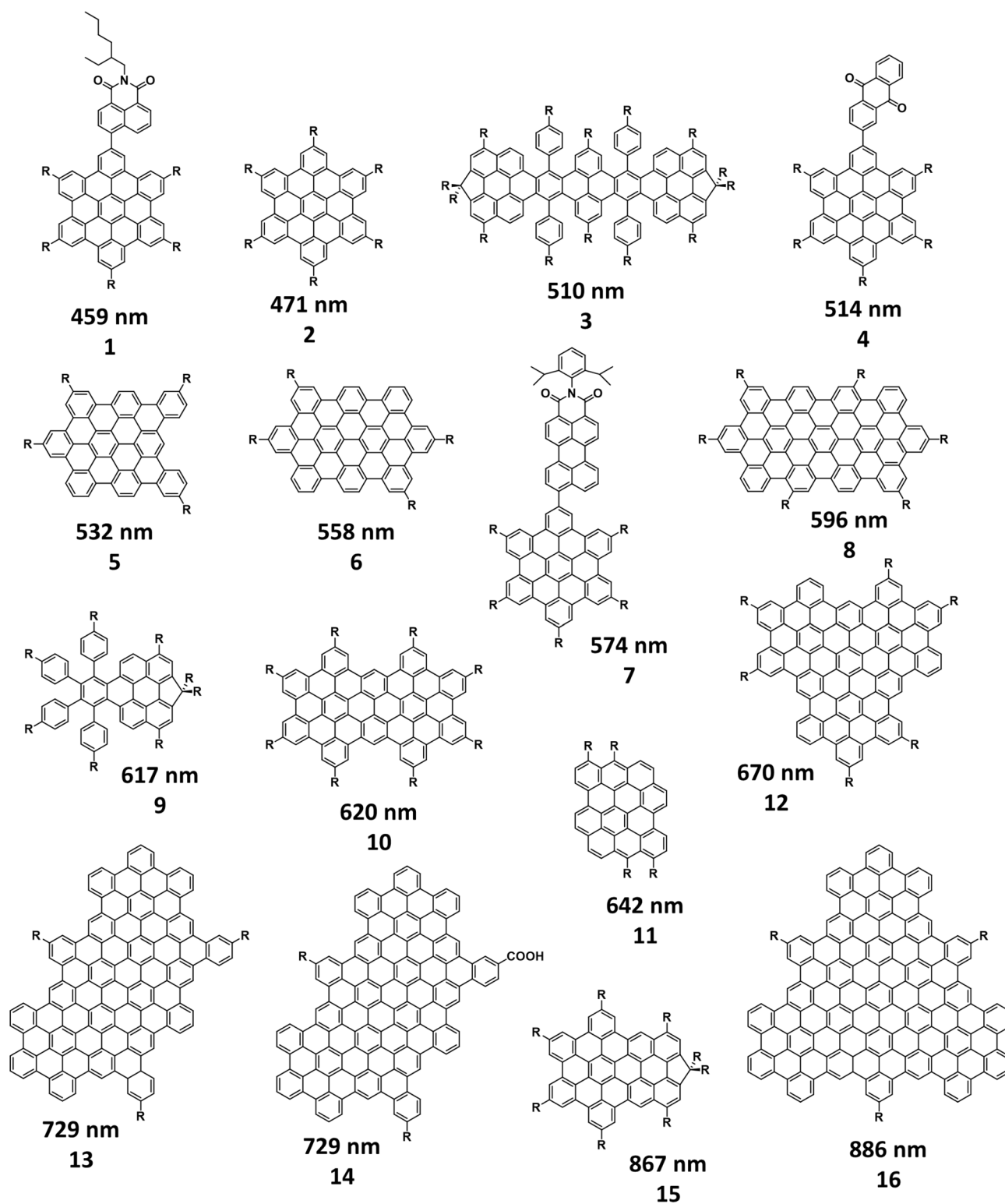
Excitons in nanographene materials exhibit exciton binding energies ( $E_b$ ) that are much larger than the available room temperature thermal energy ( $k_b T \sim 26$  meV), resulting in low efficiency of spontaneous exciton dissociation into free charge carriers. Theoretical studies have shown that  $E_b$ 's are closely related to the exciton size in GNRs, which are in turn directly related to the GNR width  $w$  (Zhu and Su 2011).

Figure 10 shows that the binding energies range from  $\sim 450$  meV for wide GNRs to  $\sim 2.5$  eV for narrow GNRs. Interestingly, the dependence of  $E_b$  (and exciton size) on the GNR width follows the same trend as the energy gap discussed earlier. For the same GNR width, the  $3p+2$  family exhibits smaller  $E_b$  values than the member of the  $3p$  family. Similar computational studies have been performed for GQDs where many-body effects (interactions between electron and hole) in confined systems are taken into account to yield a quasiparticle gap which is used in the calculation of  $E_b$ . For example, Wang et. al. produced a computational study on GQDs of varying size and edge and report  $E_b$  values larger than 1 eV, which are expected and larger than  $E_b$ 's in carbon nanotubes and GNRs due to the higher degree of quantum confinement in GQDs. The authors also report that, generally, GQDs exhibit a decrease in  $E_b$  as the lateral size of the GQD increases, with exceptions to this rule stemming from symmetry effects as discussed earlier in this review (Li et al. 2015c).

Experimental  $E_b$  values in GNRs confirm computational predictions discussed above. For example,  $E_b$  has been determined for 1.7 nm wide GNR **23** (Scheme 1) using ultrafast THz spectroscopy (Tries et al. 2020). Using 40 fs laser pulses, the excitons and/or charge carriers are generated along the GNRs. Then, a THz probe beam is used to distinguish between excitons and free carriers, based on the different response that these species exhibit in the frequency-resolved conductivity. When a low-energy pump beam is used (1.63 eV), only excitonic states are formed (Fig. 11). However, when a higher energy pump beam is used (3.1 eV) charge-carriers are formed. By varying the energy of the pump-beam, the authors found that  $E_b = 700$  meV, which is similar to the theoretically calculated value of 550 meV. The authors further investigated the dynamics of charge carriers and excitons in GNRs and found that charge carriers recombine quickly to form excitons (0.8 ps), while exciton lifetimes are relatively long-lived ( $> 100$  ps). Exciton binding energy of a GNR (**21** in Scheme 1) was determined computationally using the ab initio GW plus Bethe–Salpeter (GWBS) method. The binding energy is determined by taking the



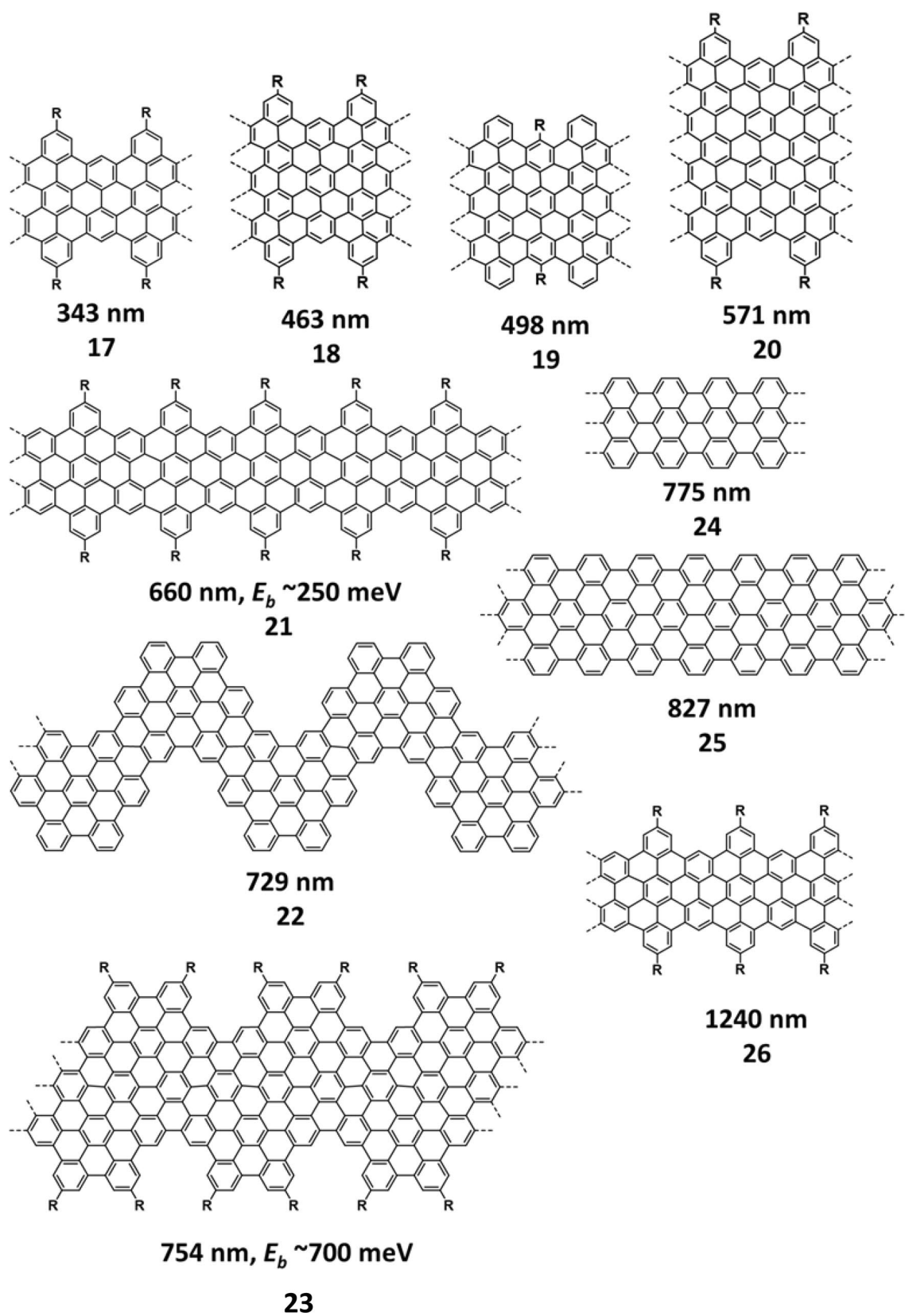
**Fig. 10** **a** Exciton binding energy,  $E_b$ , as a function of GNR width,  $w$ . **b** Exciton binding energy as a function of exciton size,  $L$  (Zhu and Su 2011)



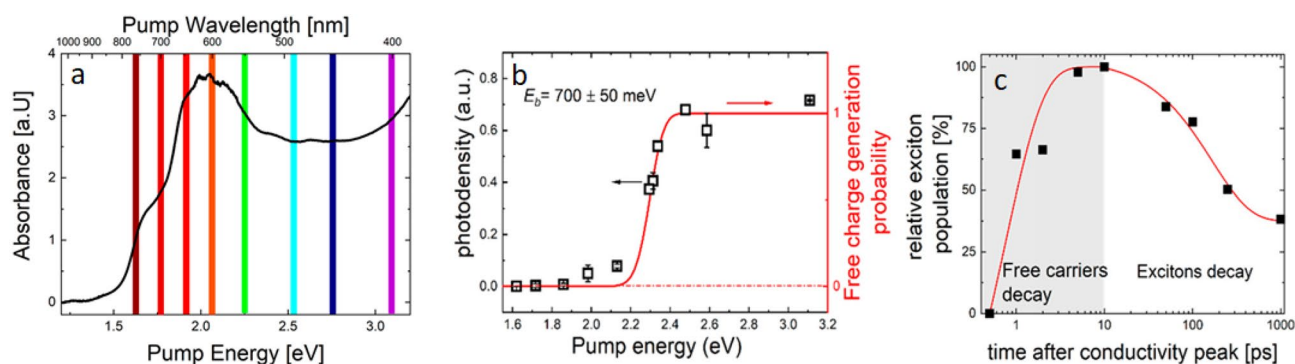
**Scheme 1** Energy gaps for an assortment of (1–16) GQDs and (17–26) GNRs, reported in units of photon wavelength. Exciton binding energy,  $E_b$ , is reported for selected structures (Yan et al. 2011; Jensen et al. 2013; Narita et al. 2014; Denk et al. 2014; Sun et al. 2015;

Soavi et al. 2016a, b; Keerthi et al. 2016; Chen et al. 2017; Paternò et al. 2017; Deilmann and Rohlfing 2017; Zhu et al. 2018; Hu et al. 2018; Huang et al. 2018; Ji et al. 2019; Xu et al. 2019; Han et al. 2020; Tries et al. 2020; Zou et al. 2020)





Scheme 1 (continued)



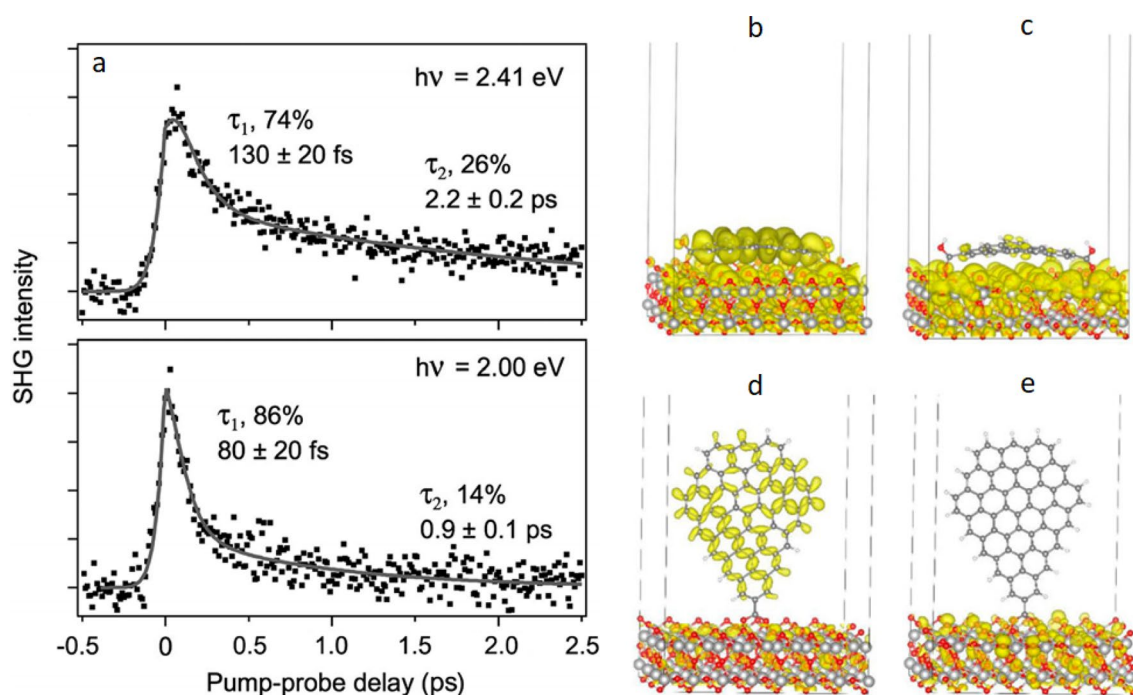
**Fig. 11** **a** UV-vis absorption spectrum of GNR **23** with excitation wavelengths highlighted in color. **b** Maximum of real conductivity signal as a function of excitation photon energy. The signal sharply rises when the exciton is dissociated into free charge carriers. **c** Time

profile for the rise and decay of the real conductivity signal (free carrier response) and decay of the imaginary conductivity signal (exciton response) (Tries et al. 2020)

difference between the GW quasiparticle bandgap and the GW-BS excitonic transition energy. The resulting giant binding energy was found to be  $\sim 1.5$  eV, consistent with what is expected for excitons in GNRs (Soavi et al. 2016a). Here, the same approach was used to computationally determine the exciton binding energy in another GNR (**24** in Scheme 1). The binding energies for the  $E_{11}$  and  $E_{22}$  excitations (lowest energy, allowed excitonic transitions) were reported as 1.8 and 1.4 eV, respectively, and correspond to quasi-1D excitons that are fully delocalized along the GNR width and spatially distributed along the ribbon axis (Denk et al. 2014). GNR **24** deposited on an Au(111) surface exhibits a decrease in exciton binding energy from 1.8 to  $0.160 \pm 0.060$  eV due to substrate polarization effects and strong electronic coupling between the GNR and gold substrate (Bronner et al. 2016).

Surprisingly, the experimentally obtained  $E_b$  values for GQDs are significantly lower (0.1–0.6 eV) (Yuan et al. 2018, 2020; Ji et al. 2019) than those predicted by theory ( $\sim 1.2$  to 1.9 eV) (Li et al. 2015b, c). For example,  $E_b$  values for two types of GQDs were obtained using temperature-dependent PL lifetimes (at higher temperatures, thermal energy from the environment causes excitons to dissociate into charge carriers, resulting in shorter PL lifetimes) and the values in the 100–150 meV range were obtained (Yuan et al. 2018, 2020). Somewhat larger values were obtained for indium-doped tin oxide (ITO)-tethered GQDs, where  $E_b$  was determined using spectroelectrochemical methods (Ji et al. 2019). The reasons for the observed mismatch could be associated with the experimental techniques used in these studies. Specifically, the PL lifetime method assumes that the lifetime decrease is associated with the exciton dissociation into charge carriers, which may not be the case. A more accurate analysis would involve the direct detection of charge carriers using THz spectroscopy.

Electron transfer from photoexcited GQDs to transition metal-based semiconductors has been investigated previously by several groups (Manga et al. 2009; Elliott et al. 2016; Long et al. 2017; Shan et al. 2019; Han et al. 2020; Yan et al. 2020; Singh et al. 2020a). Generally, two types of hybrid structures have been explored, where one involves GQDs attached to the surface of metal oxide nanoparticles ( $\text{SnO}_2$  or  $\text{TiO}_2$ ) and another is related to 0D/2D van der Waals heterojunctions composed of zero-dimensional GQDs and two-dimensional  $\text{MoS}_2$  or graphene. In all studies, the effect of GQD size on the dynamics of photoinduced electron transfer has been explored. All studies indicate that the hot electron injection takes place from photoexcited GQDs. For example, Fig. 12a shows the time-resolved second harmonic generation (SHG) signal, which is proportional to the number of charges that are photogenerated, measuring the electron transfer from excited GQD to  $\text{TiO}_2$ . The growth of the signal occurs within the laser pulse (resolution of 60 fs), indicating that the charge injection into  $\text{TiO}_2$  occurs at the sub 15 fs timescale. This injection time is much faster than the hot electron lifetimes in GQDs (up to 10 ps) (Williams et al. 2013). Specifically, the hot electron lifetimes were found to increase as the GQD size is decreased and this behavior is explained by the “phonon bottleneck” effect, where the energy spacing in quantum-confined systems becomes larger than the phonon frequencies, resulting in the lower efficiency of relaxation of higher-energy excited states. Computational studies illustrated in Fig. 12b–e have explored the effect of GQD/ $\text{TiO}_2$  bonding on the efficiency of electron transfer (Long et al. 2017). The covalent binding through carboxylate linker was found to lead to weak electronic coupling, while strong electronic coupling and ultrafast charge injection are predicted for the through-space  $\pi$ -electron adduct, pointing to the importance of van der Waals interactions in mediating fast charge separation.



**Fig. 12** **a** Photo-induced charge transfer dynamics observed via time-resolved SHG of GQD/TiO<sub>2</sub>(110) at 300 K and pump energies of 2.41 eV (top) and 2.00 eV (bottom). Charge densities of photoexcited

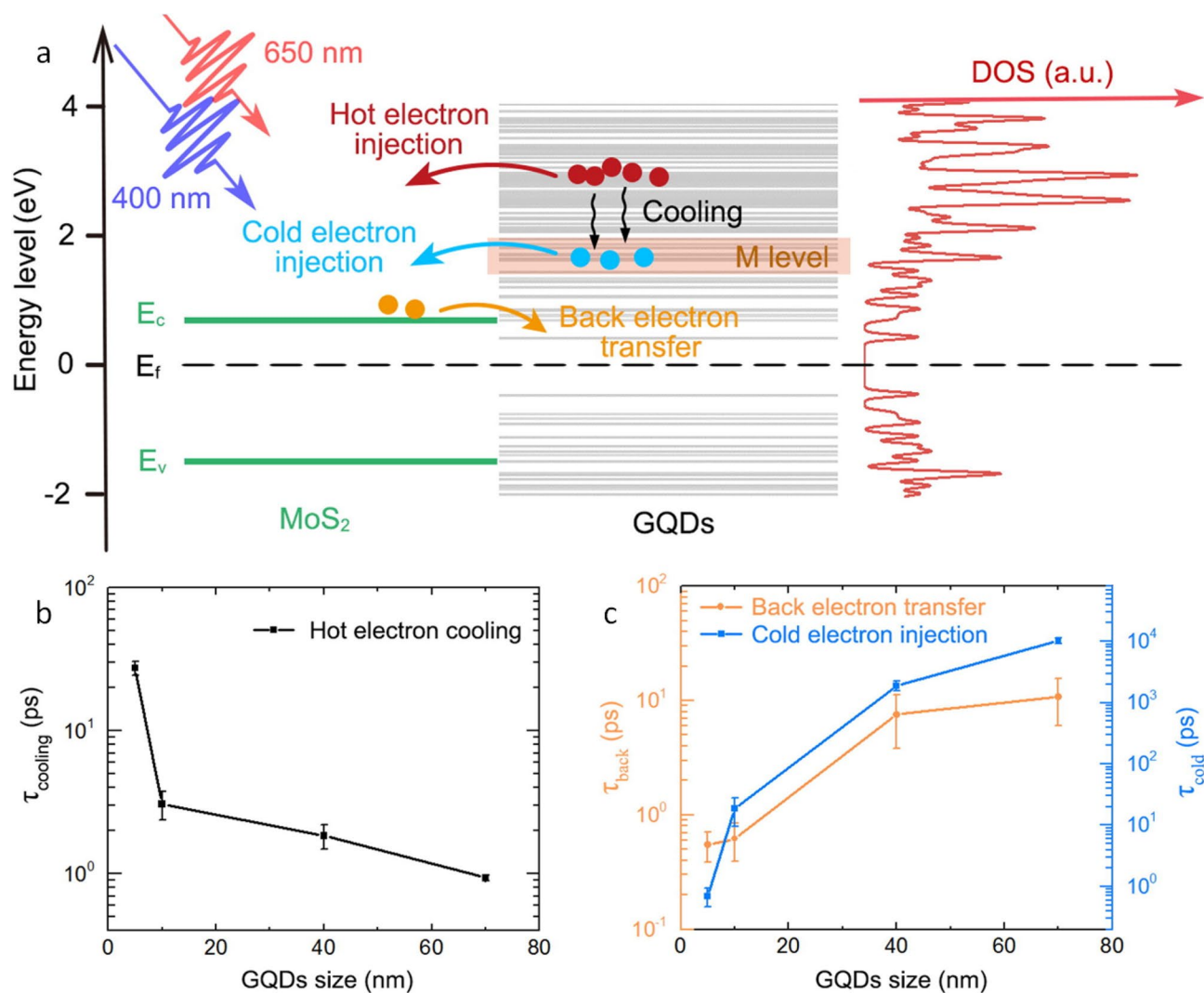
**b** donor state of F-coronene/TiO<sub>2</sub>, **c** acceptor state of F-coronene/TiO<sub>2</sub>, **d** donor state of VGQD/TiO<sub>2</sub>, and **e** acceptor state of VGQD/TiO<sub>2</sub> (Williams et al. 2013; Long et al. 2017)

Similar effects of GQD size on hot electron cooling rates was observed for GQD/MoS<sub>2</sub> hybrids (Fig. 13a) (Shan et al. 2019). In addition to the hot electron cooling dynamics, the rates of cold electron injection ( $\tau_{\text{cold}}$ ) and subsequent charge recombination ( $\tau_{\text{back}}$ ) were also found to depend on the GQD size. For example, Fig. 13b, c show that both  $\tau_{\text{cold}}$  and  $\tau_{\text{back}}$  increase with increased GQD size in GQD/MoS<sub>2</sub> hybrids, which was assigned to the change in the thermodynamic driving force for photoinduced electron transfer with the GQD size and was well modeled using Marcus theory.

Electron and energy transfer kinetics were also investigated for hybrids involving GQDs and transition metal complexes (Kim et al. 2006; Elliott et al. 2016; Umeyama et al. 2019; Singh et al. 2020a). For example, our group investigated the excited-state behavior of GQDs that contain cobaloxime-based hydrogen evolution catalysts shown in Fig. 14 (Singh et al. 2020a). We found that the excited state, localized on the GQD moiety, is readily quenched in the presence of cobaloximes. Our experimental results indicate that the quenching mechanism involves either the photoinduced electron transfer from photoexcited GQD to the cobaloxime or Dexter-type energy transfer. No charge-separated states were observed in transient absorption, indicating that the system quickly relaxes back to the ground state.

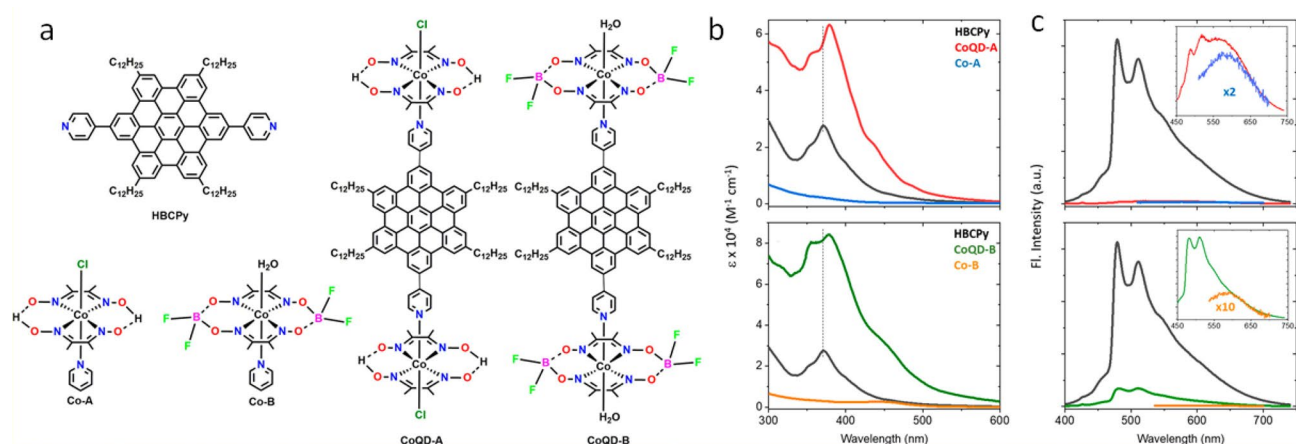
## Applications

The highly tunable photophysical properties of nanographenes make them promising materials for light-emitting diode (LED) applications. Furthermore, the low cost and low toxicity of nanographenes, combined with their high thermal and photo-stability makes them ideal LED phosphors. For indoor lighting applications, warm LEDs are needed to minimize eye fatigue effects. Warm LEDs are made using UV-LEDs coated with broad-emission red, green and blue tricolor phosphors. Given that GQDs can be photoexcited in the UV-region and they tend to exhibit broad emission spectra, high PL QYs and tunable emission wavelengths, they have been successfully applied as blue, green and red phosphors for warm LED applications (Qu et al. 2016; Wang et al. 2017). For example, three GQD phosphors that emit in blue (with PL QY = 72%), green (PL QY = 71%) and red (PL QY = 50%) were used to fabricate warm LED with a luminous efficiency of 31.3 lmW<sup>-1</sup> at 20 mA current (Wang et al. 2017). In other LED applications, such as displays, phosphors should exhibit narrow emission bands. Until recently, GQDs had limited performance in such devices, because of their broad emission characteristics. However, narrow emission profiles were obtained by careful control over the GQD chemistry



**Fig. 13** **a** Band diagram of GQDs/MoS<sub>2</sub> heterostructure (left), calculated eigen states (middle), and density of states of GQDs (right). **b** Hot electron cooling lifetime for GQDs of varying size. **c** Lifetimes of

cold electron injection and back electron transfer in heterostructures (Shan et al. 2019)



**Fig. 14** **a** Structures of some cobaloxime-based hydrogen evolution catalysts. **b** Absorption and **c** emission spectra of the structures on the left, showing quenching on photoexcitation (Singh et al. 2020a)

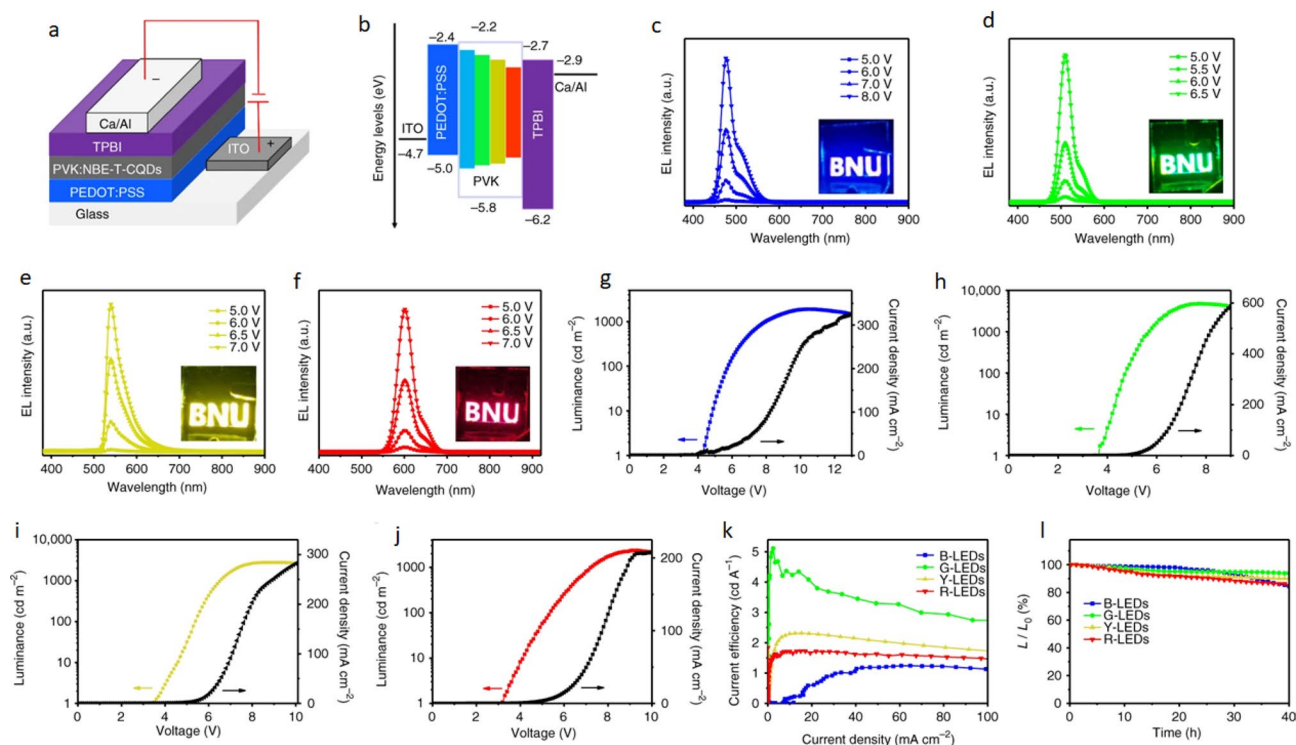


(Yuan et al. 2018, 2020). For example, the presence of carboxylate groups on the edges of GQDs was found to cause the emission broadening due to the changes in the  $\pi$ -delocalization of the chromophores as the carboxylate group rotates in and out of plane of the nanographene. This paper reports first HBC based LED which shows electroluminescence peak at 490 nm with a FWHM of 20 nm. Amination of GQD edges to remove the carboxylate groups has produced deep-blue LEDs with 70% QY, among the highest QY values of GQDs to date and comparable to the highest performing  $\text{Cd}^{2+}/\text{Pb}^{2+}$ -based emitters (Yuan et al. 2020). In another study, an exceptional narrowband emission (FWHM = 30 nm) was achieved using T-GQDs, and highest QYs to date were reported ( $\text{QY}_{\text{blue}} = 66\%$ ,  $\text{QY}_{\text{green}} = 72\%$ ,  $\text{QY}_{\text{yellow}} = 62\%$ , and  $\text{QY}_{\text{red}} = 54\%$ , Fig. 15) (Yuan et al. 2020).

The impressive emissive properties of nanographenes make them promising contenders for low-threshold lasers with long operational times (Yuan et al. 2019b; Bonal et al. 2019; Zou et al. 2020) and optical sensors (Sun et al. 2013; Ananthanarayanan et al. 2014; Shi et al. 2015; Song et al. 2016; Hai et al. 2018; Xu et al. 2018). For example, T-GQDs in Au–Ag bimetallic porous nanowires have shown lasing application with performances superior than perovskites

and traditional colloidal semiconductor QD based random lasers. The prepared blue, green and red random lasers showed a lasing threshold of 0.087, 0.052 and 0.048  $\text{mJ}/\text{cm}^2$  along with corresponding FWHMs of 0.9, 0.37 and 0.82 nm, respectively (Yuan et al. 2019b). Additionally, distribution feedback lasers based on zigzag-edged nanographenes have been demonstrated to operate at a threshold as low as 11  $\mu\text{J}/\text{cm}^2$  with a narrow FWHM of 0.13 nm (Bonal et al. 2019). On the biological sensing front, functionalized GQDs allow binding with the target analyte through various kinds of interactions, such as electrostatic attraction or  $\pi$ - $\pi$  conjugation, results in the quenching of PL (Hai et al. 2018). For example, chemically modified GQDs have been demonstrated to sense biological  $\text{Fe}^{3+}$  (Ananthanarayanan et al. 2014),  $\text{Ni}^{2+}$  (Xu et al. 2018),  $\text{Cu}^{2+}$  (Sun et al. 2013), and  $\text{H}^+$  ions (Song et al. 2016). Challenges to be overcome in the biological application of nanographenes are being studied and include biocompatibility, selectivity, and cytotoxicity.

Nanographenes have been used as photoactive materials in photovoltaics with limited success (Qin et al. 2015). Due to high exciton binding energy of nanographene materials, photovoltaic nanographene cells are made as bulk heterojunctions with appropriate electron donors or acceptors. These blends ensure efficient charge separation at interfaces



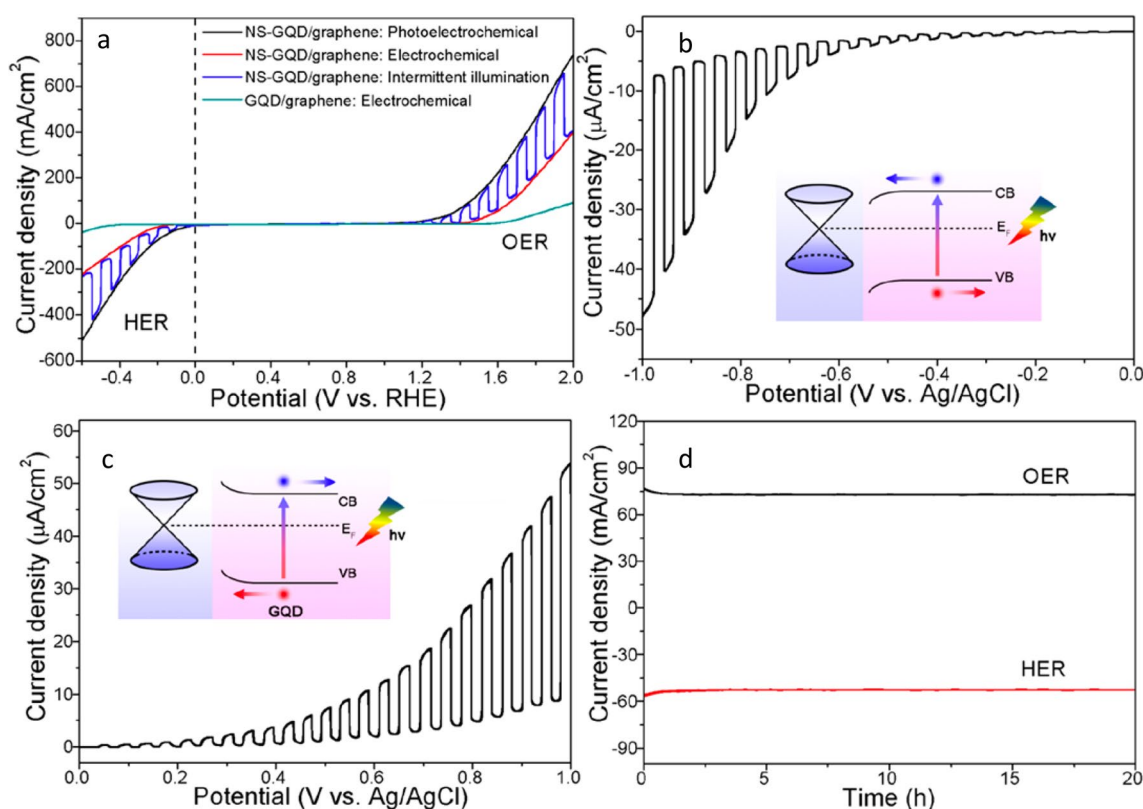
**Fig. 15** **a** GQD-based LED device structure. **b** Energy level diagram of LED device. Electroluminescence of LEDs based on **c** blue, **d** green, **e** yellow, and **f** red emitting triangular GQDs at different bias voltages. Maximum luminance-current-voltage characteristic of **g**

blue, **h** green, **i** yellow, **j** and red emitting triangular GQDs. **k** Current efficiency versus current density and **l** stability plots of the GQD-based LED devices (Yuan et al. 2018)

and 3–4% power conversion efficiencies can be achieved. Nanographenes have also been used as “photon management” chromophores for photovoltaic devices (Khan and Kim 2018). Namely, GQDs with large Stokes shifts and high PL QYs were utilized to down-convert blue photons for use in Cu(In,Ga)Se<sub>2</sub> solar cells. This conversion of blue photons to lower energy photons minimizes the efficiency loss associated with the parasitic absorption of blue light by ZnO and CdS windows and buffer layers in these devices. Furthermore, GQDs have been shown to uplift the Fermi level of perovskite-based films and improving the charge separation in them resulting in an increase of solar cell efficiency by 2.7% (Gan et al. 2019).

Nanographenes are also being developed for application in photocatalysis, such as solar water splitting and carbon dioxide reduction (Yan et al. 2018, 2020; Tsai et al. 2020). For example, efficient photoelectrochemical water splitting was achieved using 0D/2D van der Waals heterojunctions composed of zero-dimensional GQDs and two-dimensional graphene (Yan et al. 2020). The energy gap of GQDs was tuned to be ~2 eV to ensure the most efficient harvesting of the solar spectrum and sufficient energy to drive the water

splitting. The performance of these heterojunctions in photoelectrochemical water splitting is shown in Fig. 16. The presence of several-fold current enhancement is observed under illumination, indicating efficient photocatalysis. The GQD-graphene hybrids in the aforementioned study exhibited a fast Volmer-Heyrovsky mechanism for hydrogen evolution and a fast two-step mechanism for oxygen evolution. The performance of GQDs in photocatalytic water splitting can be optimized via chemical tuning of the GQD. For example, Yan and coworkers demonstrated a systematic approach to engineering bandgaps in GQDs for photocatalytic water splitting and CO<sub>2</sub> reduction in 2018 (Yan et al. 2018). Incorporation of a Z-scheme mechanism was achieved using GQD materials modified via  $\pi$ -system extension to introduce either p- and n-type semiconducting domains. Upon excitation with visible light (420–800 nm), an electron is generated in the p-type domain (which reduces CO<sub>2</sub> to methanol) and a hole forms in the n-type domain (which oxidizes water to produce O<sub>2</sub>). The authors note that, while the photocatalytic performance of their GQDs are not competitive with other common photocatalysts in industry (H<sub>2</sub> yield of 130  $\mu\text{mol h}^{-1}$ , and methanol yield of 0.695  $\mu\text{mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ ),



**Fig. 16** Electro- and photoelectrochemical water splitting results of GQDs. **a** Hydrogen evolution and oxygen evolution linear scan curves of heteroatom nitrogen/sulfur-containing GQDs/graphene hybrid structures in 1.0 M KOH with Xe lamp illumination (black) intermittent illumination (blue), and with no illumination (red). For

reference, electrochemical performance of GQD/graphene (green) is also shown. Cathodic **b** and anodic **c** current densities of NS-GQD/graphene in ethanol with 0.1 M KOH with intermittent illumination. **d** HER and OER current densities with respect to time under Xe lamp illumination (Lin et al. 2018) (Yan et al. 2020)

optimization of the GQD for photocatalysis is a necessary and important step towards synthesizing GQD-hybrid materials that exhibit competitive photocatalysis.

## Future directions

Our short review summarizes a range of interesting photophysical properties of nanographenes and their applications in optoelectronic and photocatalytic applications. One particular area that has shown great promise, but has not been explored in great detail, is photocatalysis. With recent developments in bottom-up wet chemistry synthetic methods, photocatalytic nanographene materials can be readily made from GNRs or GQDs and molecular transition metal catalysts for water splitting, carbon dioxide reduction, or any other oxidation/reduction reaction. Tunable energy gaps of nanographenes, along with efficient exciton and charge carrier mobilities in these materials make them ideal platforms for photocatalysis. Furthermore, nanographenes can be solubilized using appropriate pendant groups, enabling “wireless” photocatalysis in solution. Future studies investigating structural factors that control light harvesting, photoinduced charge separation/recombination and subsequent bond forming and breaking steps will enable a new generation of nanographene photocatalysts.

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## Declarations

**Conflict of interest** The authors declare no competing financial interest.

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