

Toward Multifunctional Wet Chemically Functionalized Graphene—Integration of Oligomeric, Molecular, and Particulate Building Blocks that Reveal Photoactivity and Redox Activity

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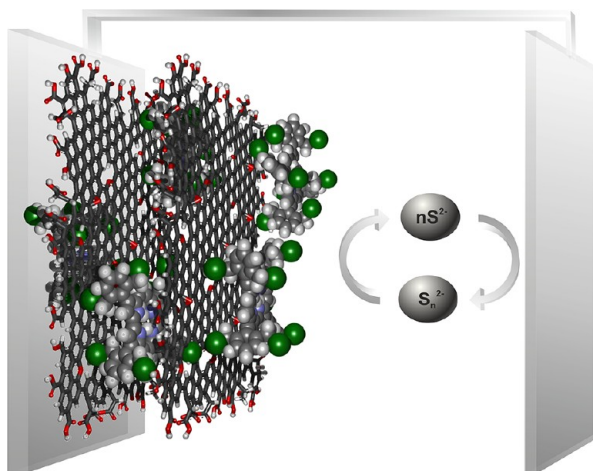
CONSPECTUS

Many technological applications indispensable in our daily lives rely on carbon. By altering the periodic binding motifs in networks of sp^3 , sp^2 , and sp -hybridized carbon atoms, researchers have produced a wide palette of carbon allotropes. Over the past two decades, the physicochemical properties of low-dimensional nanocarbons, including fullerenes (0D), carbon nanotubes (1D), and, most recently, graphene (2D), have been explored systematically.

An entire area of research has focused on the chemistry of 1D nanocarbons, particularly single-wall carbon nanotubes. These structures exhibit unique electronic, mechanical, and optical properties. These properties are, however, only discernible for single-wall carbon nanotubes that are debundled, individualized, and stabilized, often in solution. Most prominently, they are small band gap, p -type semiconductors or metals with conductances that reach ballistic dimensions. These structures can have poor solubility in many media, and large bundles can originate from attractive interactions such as π - π stacking and London dispersion forces. Therefore, both covalent and noncovalent modifications of single-wall carbon nanotubes have emerged as powerful approaches to overcome some of these problems. Noncovalent functionalization is especially useful in improving the solubility without altering the electronic structure.

We expect that many of the strategies that have recently been exploited and established in the context of 1D nanocarbons can be applied to the chemistry of 2D nanocarbons, especially graphene. Two-dimensional nanocarbons are currently attracting extensive attention due to their striking mechanical, optical, and electrical features. Nanocarbons that are a single atom thick are gapless semiconductors and exhibit electron mobilities reaching values of up to $15000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. Researchers have made rapid progress in the covalent and/or noncovalent functionalization of graphene with photoactive and/or redox active building blocks.

In this Account, we summarize our work on the integration of photoactive and/or redox active building blocks, including oligomers, molecules, and particulates, onto graphenoid materials to yield multifunctional electron donor–acceptor conjugates and hybrids. Intriguingly, we produce graphene in the form of single-layer, bilayer, and multilayer graphene through the exfoliation of graphite by surface active agents. The exfoliation occurs through π - π , hydrophobic, van der Waals, electrostatic, and charge transfer interactions, and the surface active agents also serve as versatile anchor groups. We studied the electronic interactions in terms of photoactivity and/or redox activity in depth by steady-state and time-resolved spectroscopy. Finally, we present examples of proof-of-principle solar energy conversion devices.



Carbon is the key to many technological applications that have become indispensable in our daily life. Altering the periodic binding motifs in networks of sp^3 -, sp^2 -, and sp -hybridized carbon atoms is the conceptual starting point for a wide palette of carbon allotropes.¹ To this end, the past two decades have served as a test-bed for measuring the physicochemical properties of low-dimensional nanocarbons with the advent of fullerenes (0D),² followed in chronological order by carbon nanotubes (1D),³ and, most recently, by graphene (2D).⁴

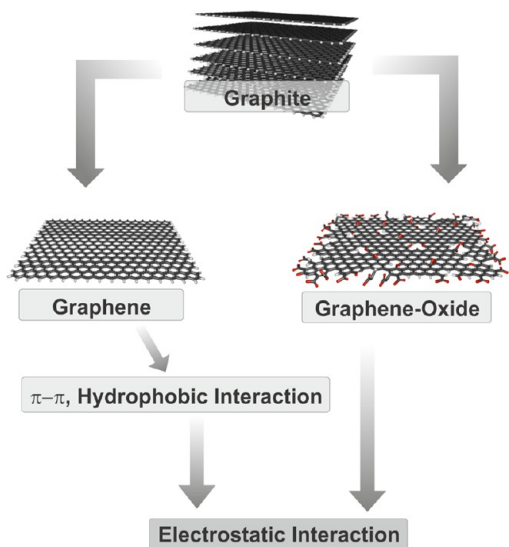
An entire area of research has focused on the chemistry of 1D nanocarbons, namely carbon nanotubes, in general, and single-wall carbon nanotubes, in particular. They exhibit unique structural, electronic, mechanical, and optical properties.⁵ These properties are, however, only discernible for single-wall carbon nanotubes that are debundled, individualized, and stabilized in, for example, solution. Most prominently, they are either small band gap, p -type semiconductors or metals with conductance that reaches ballistic dimensions. Their poor solubility in common media is, nevertheless, a major concern. Here, the large bundles that originate from attractive interactions such as π - π stacking and London dispersion forces are aspects that require careful attention. In this respect, the covalent and noncovalent modification of single-wall carbon nanotubes has emerged as a powerful approach to overcome some of these bottlenecks and to realize their full potential.⁶ A real asset is the noncovalent functionalization, as it assists in improving the solubility without altering the electronic structure.⁷

Likewise, 2D nanocarbons, namely graphene, are currently attracting extensive attention due to their striking mechanical, optical, and electrical features.⁸ In the case of a single-atom-thick nanocarbon, it is a gapless semiconductor and exhibits electron mobilities reaching values of up to $15000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. Importantly, exfoliated, individualized, and stabilized layers of graphene are required to realize such values.

Taking the aforementioned into concert, many aspects that have recently been exploited and established in the context of 1D nanocarbons are expected to be applicable to the chemistry of 2D nanocarbons, especially toward the realization of single-layer graphene. As matter of fact, rapid progress in the covalent and/or noncovalent functionalization of single-layer graphene with photoactive and/or redox active building blocks reflects the leading edge of this field in the area of contemporary research.⁹

In this Account, we highlight the exciting developments in the synergistic use of graphene as a state-of-the-art building block in electron donor–acceptor conjugates and hybrids *en-route* toward innovative solar energy conversion systems (Scheme 1). Within such interdisciplinary concepts, single-layer graphene-like single-wall carbon nanotubes offer a unique

SCHEME 1. Exfoliation of Graphite by Activation through Ultrasonication and Concomitant Functionalization (i.e., left hand side) or Oxidation to Graphene Oxide (i.e., right hand side), Both Enabling Electrostatic Interactions



platform for exploring structural parameters, fine-tuning critical physicochemical parameters, and gaining full control over the chemical composition and mutual interactions.¹⁰ Particular emphasis is placed on elucidating covalent and noncovalent routes for graphene oxide (GO) and single-layer graphene. This Account will be rounded off by a few examples that illustrate the implementation of GO and single-layer graphene in solar energy conversion devices.

Covalent versus Noncovalent Approaches

A fair amount of work concentrates on wet-chemical routes toward the covalent and the noncovalent functionalization of the basal plane in graphene rather than in graphite. This is primarily meant to overcome the obstacles associated with the low dispersibility, rather poor processability, limited stability, etc., of graphene sheets in virtually any given solvent.

A leading route implies the exfoliation/functionalization of graphite flakes through a number of different oxidation reactions yielding GO,¹¹ subsequent chemical modification,¹² and, ultimately, reduction to obtain single-layered, functionalized reduced graphene oxide (rGO). One of the major disadvantages of this procedure is the modification of the intrinsic electronic properties of graphene when transforming graphite into GO and into rGO.¹³ Still, owing to the great stability and the reasonable dispersibility of GO and rGO in organic solvents and water, they have widely been applied as starting materials to link functional groups (i.e., light harvester,¹⁴ electron donors,¹⁵ electron acceptors,¹⁶ etc.). In addition to the chemical conversion of functional GO

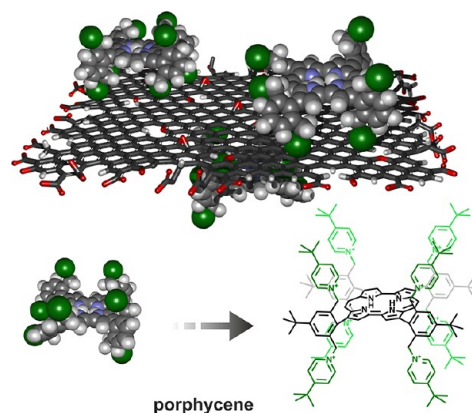
and rGO groups—including $-\text{COOH}$, $-\text{C}=\text{O}$, $-\text{COOR}$, $-\text{COH}$, etc.—a myriad of noncovalent forces, which are based, among others, on $\pi-\pi$ and electrostatic interactions, hereby play a dominant role.¹⁷

Quite a different route is initiated through electron transfer reactions between alkali metals and/or alloys and graphene layers in the starting graphite. The latter is followed by the subsequent intercalation of the correspondingly generated cationic species into the reduced graphite crystal to afford novel graphite intercalation compounds with intriguing features.¹⁸ To this end, liquid exfoliation¹⁹ and electrophilic addition with, for example, alkyl halides²⁰ and diazonium salts²¹ yield covalently functionalized graphene of very high quality. As a matter of fact, annealing the covalently functionalized graphene, namely selective defunctionalization, assists in recovering the intrinsic sp^2 -hybridized carbon network of nearly perfect graphene.

In stark contrast to the case of the aforementioned route, liquid-phase exfoliation of graphite by means of mild sonication in solvents such as *N*-methyl pyrrolidone (NMP) has attracted a great deal of attention.²² In fact, it has evolved as a versatile means to obtain stable dispersions of nonmodified graphene. Notable is that the resulting graphenoid material, which is, however, present in the form of few-layer graphene, is readily employed in further chemical modification/functionalization reactions.²³ In particular, the covalent linkage of nonmodified graphene obtained by liquid-phase exfoliation of graphite has been demonstrated in cases where solvent mediated suspensions of few-layer graphene were subjected to cycloaddition²⁴ and radical and nitrene addition.²⁵

Finally, the noncovalent functionalization route with functional groups (i.e., surfactants) should be mentioned. It enables the direct functionalization of graphite, on one hand, and its concomitant exfoliation, on the other hand. Please note that the functional groups, which are simply immobilized by means of weak dispersive forces, are displaceable in solution.²⁶ To this end, just washing with pure solvents and providing a different functional group (i.e., light harvester, electron donors, electron acceptors, etc.²⁷) in reasonable excess are sufficient measures to impact and shift the underlying equilibria from immobilizing the surfactant to immobilized light harvester, electron donors, electron acceptors, etc. For example, pyrene based surfactants have been shown to overcome the intrinsically strong $\pi-\pi$ interactions between graphene layers that are operative in full force in graphite.²⁸ In turn, individual sheets of single-layer graphene etc. are peeled

SCHEME 2. Schematic Representation of Noncovalently Functionalized GO by Means of Electrostatic Interactions with a Positively Charged Porphycene (Porphycene⁺)



off and stabilized in solution by van der Waals and/or hydrophobic interactions.²⁹ Overall, such a procedure opens routes to hybrids that exhibit even more exciting features than graphene. In the context of the current Account, a notable example is the control over the doping level in graphene to adjust the conductivity and the resulting charge carrier type transport. In particular, an electron accepting TCNQ has been used in a solution process³⁰ to *p*-dope graphene.³¹

Covalent Approach to Graft Molecular Building Blocks to Graphene Oxide (GO)

GO, in which van der Waals interactions between individual layers are overcome by Coulombic repulsions, is available in scalable amounts. Soluble GO material is *en vogue* for grafting molecular building blocks following both covalent and noncovalent methodologies. In the context of covalent chemistry, the functional groups in GO, namely $-\text{COOH}$, $-\text{OH}$, etc., are highly versatile in terms of esterification or amidation reactions. For instance, optically active porphyrins were attached to GO, affording unique electron donor–acceptor conjugates.³² In addition to electron donating porphyrins, linking electron accepting fullerenes was also realized by a similar chemistry.¹⁶ Notable also is an approach, in which rGO was subjected to chemical modification with the objective to link photoactive groups.¹⁵ Here, azide alkyne click reactions offer an exciting new approach to functionalized GO. Initially, azide groups are introduced to GO through sodium azide, which then undergoes the click reaction with primary alkynes to form triazoles. Depending on the alkyne substituents, different functional groups may be attached to GO. Azides may also be reduced to amines, which allows performing typical carbonyl condensation reactions.³³ Alternatively, diazonium radicals bearing

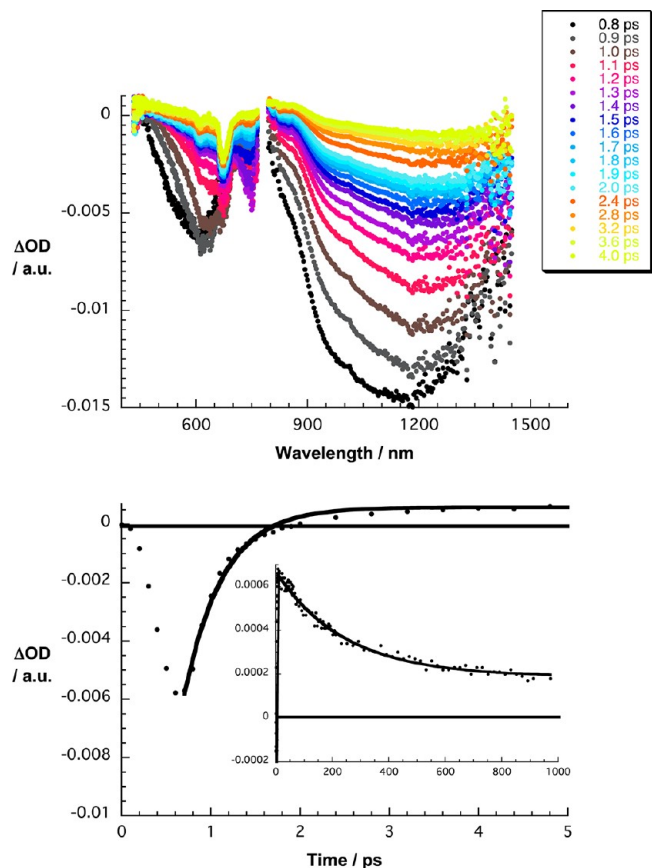


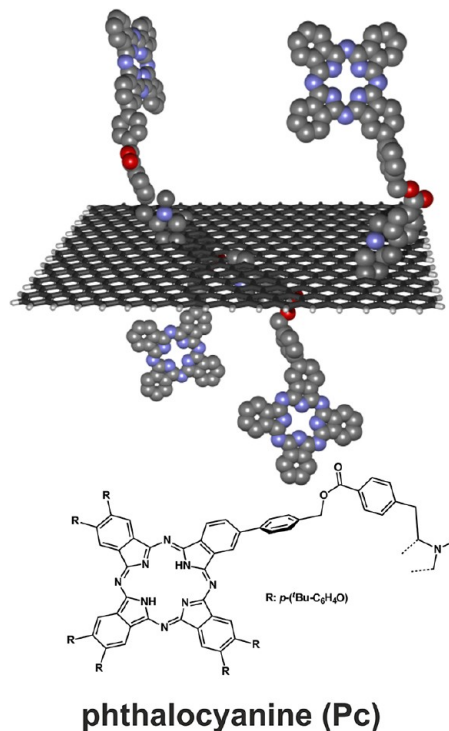
FIGURE 1. (Upper part) differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump-probe experiments (387 nm) of few-layer graphene/*n*-type PPV ZnPc in THF with several time delays between 0.8 and 4 ps at room temperature—time evolution from black to red to blue and orange. (Lower part) time-absorption profiles (0–5 ps) of the spectra shown above at 850 nm monitoring the forward electron transfer—the inset shows the time-absorption profile (0–1000 ps) of the spectra shown above at 850 nm monitoring the backward electron transfer.

alkynes are introduced to rGO in a first step before photoactive ruthenium complexes or porphyrins are added. The latter assisted in synthesizing remarkable photoconversion systems.¹⁴

Noncovalent Approach To Immobilize Molecular Building Blocks onto Graphene Oxide (GO)

Next to the aforementioned chemical modification, –COOH in GO constitutes a versatile scaffold for exploring noncovalent methodologies. On one hand, GO dissolves readily under basic conditions in aqueous media. On the other hand, considering that the surface of GO is covered with negatively charged ionic head groups, van der Waals and electrostatic forces are utilizable to complex oppositely charged electron donors and/or acceptors—perylene, pyrene, etc.³⁴ In our assays, a water-soluble

SCHEME 3. Schematic Representation of Covalently Functionalized Graphene (i.e., few-layer graphene) by Means of a 1,3-Dipolar Addition Reaction with a Phthalocyanine (Pc)

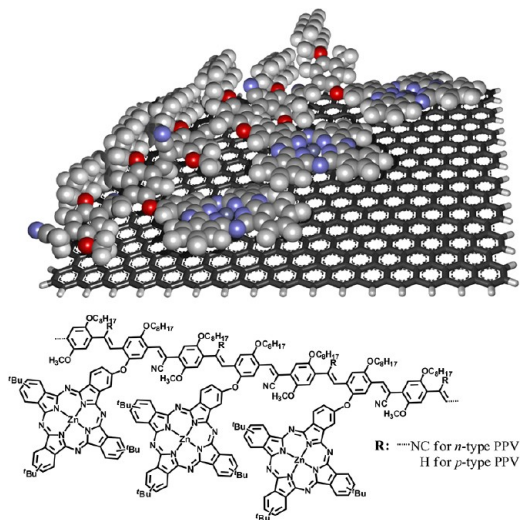


porphycene—2,7,12,17-tetrakis(2',6'-bis(*N*-methylene(4''-*tert*-butylpyridinium))-4'-*tert*-butylphenyl) porphycene (porphycene⁺)—was selected as an electron accepting building block for the development of graphene oxide based electron donor–acceptor hybrids; see Scheme 2.³⁵ Decisive evidence for the proposed interactions, that is, electrostatic association and excited state deactivation, came from assays that are based on steady-state and time-resolved fluorescence measurements. Both assays gave rise to significant quenching of the porphycene⁺ centered fluorescent features—an indication for energy and/or electron transfer deactivation. Such a performance is an asset for constructing novel photoelectrodes—*vide infra*.

Covalent Approach To Graft Molecular Building Blocks to Graphene

Covalent functionalization of few-layer graphene with metal-free phthalocyanines (Pc) was achieved in three steps.³⁶ First, graphite flakes were sonicated in NMP. Second, 1,3-dipolar cycloaddition between exfoliated graphite (sonicated graphite flakes), an excess of *N*-methylglycine, and 4-formylbenzoic acid afforded modified graphene, which carries pyrrolidine rings with pending

SCHEME 4. Schematic Representation of Noncovalently Functionalized Graphene (i.e., few-layer graphene) by Means of Zinc-Phthalocyanine *para*-Phenylenevinylene Oligomers (*n*-type PPV ZnPc)



zinc-phthalocyanine *para*-phenylenevinylene oligomers

phenylcarboxylic acids. Third, an esterification reaction with alcohol-terminated metal-free Pc yielded a novel graphene–Pc electron donor–acceptor conjugate; see Scheme 3.

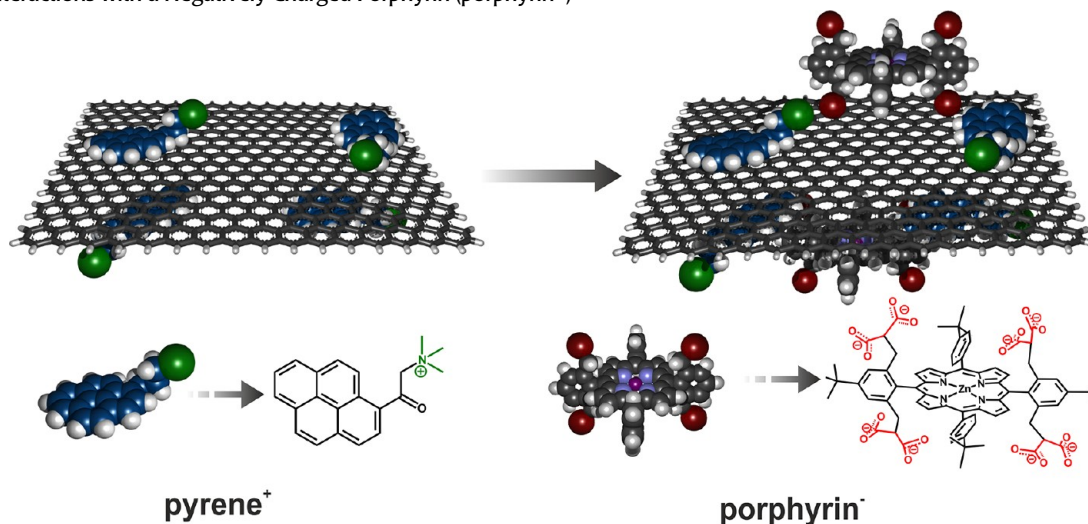
In graphene-Pc, the number of Pc's attached to the basal plane of graphene was approximated from thermogravimetric analysis as 1 per 1600 carbon atoms. The 2D-band in graphene-Pc is highly symmetric and is fit by a single Lorentzian with a FWHM of 57 cm^{-1} and exhibits a 2D/G ratio of 0.9. The latter attests the presence of strongly exfoliated graphite in the form of few-layer graphene. AFM, TEM, and HRTEM images corroborated the presence of few-layer graphene flakes with, for example, an average height of ca. 4 nm (i.e., AFM). Most of the flake sizes range from 1 to $2\ \mu\text{m}^2$, with some of them exceeding $5\ \mu\text{m}^2$. It is notable that the major drawback in terms of few-layered, regularly stacked graphene relates to the precursor material, which was obtained by mildly sonicating graphite flakes in NMP. Still, an affirmation of the electronic communication in graphene-Pc was derived from resonantly exciting at 633 nm. The detection of a Raman spectrum was only possible due to the completely quenched Pc fluorescence. In fact, a full-fledged physicochemical characterization provided the unambiguous corroboration of an ultrafast charge separation from the photoexcited Pc to few-layer graphene followed by a much slower charge recombination. A multiwavelength analysis afforded lifetimes for charge separation and charge recombination of 3.3 and 270 ps, respectively, in *N,N*-dimethyl formamide (DMF). In NMP,

the charge recombination is slightly slower with a lifetime of 340 ps.

Noncovalent Approaches To Immobilize Oligomeric and Molecular Building Blocks onto Graphene

The use of oligomeric backbones either of *p*-type (i.e., ordinary *para*-phenylenevinylene (*p*-type PPV)) or *n*-type (i.e., isonitrile functionalized *para*-phenylenevinylene (*n*-type PPV)) character has evolved as a powerful methodology for the immobilization of zinc-phthalocyanine (ZnPc) onto the basal plane of graphene; see Scheme 4.³⁷ Importantly, the latter is expected to fine-tune the Fermi level of single-layer graphene due to permanent chemical doping, that is, a redistribution of electron density as a new dark state. For example, interfacing *p*-type PPVs will raise the Fermi level into the conduction band, while *n*-type PPVs will reverse the trend, namely lower the Fermi level into the valence band. Despite a well balanced work procedure that included several cycles of stirring, temperature controlled sonication, and centrifugation, none of the PPVs resulted exclusively in single-layer graphene in THF as solvent regardless of the doping type (i.e., *n*- or *p*-type) or oligomer length (i.e., 3, 9, and 16 repeat units). Instead, a detailed Raman analysis revealed the coexistence of single-layer and few-layer graphene. More important is the strong exfoliation indicated by Raman spectroscopy of the Bernal-stacked starting material. The asymmetric 2D-band is displaced by a strongly symmetric 2D-band, where the 2D/G-ratio depends on the length of the applied oligomer; the longer the oligomer, the better the degree of exfoliation. Despite the lack of exclusive single-layer graphene, which might be doped in the dark state, evidence for interactions in the excited state and temporary chemical doping came from fluorescence and pump–probe experiments in the case of *n*-type PPV ZnPc. In particular, a quantitative quenching of the ZnPc centered fluorescence evolved in solution experiments with diluted samples, on silicon surfaces with crystallites, as well as with resonant Raman experiments (i.e., 633 nm) in the solid. These go hand in hand with the transient formation of a charge transfer state; Figure 1. The latter is based on unambiguous spectroscopic evidence of the well-established signature of ZnPc π -radical cation, that is, the oxidation of ZnPc. At this point, the electron injection into single-/few-layer graphene was postulated on the basis of a rather broad bleaching in the near-infrared with a local minimum at 1290 nm. This metastable state, in which single-/few-layer graphene features *n*-type character, is

SCHEME 5. Schematic Representation of Noncovalently Functionalized Graphene (i.e., bilayer graphene) by Means of Pyrene⁺ Followed by Electrostatic Interactions with a Negatively Charged Porphyrin (porphyrin⁻)



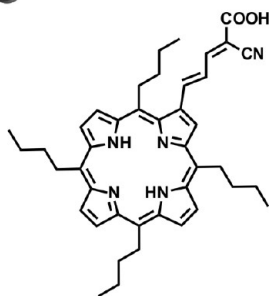
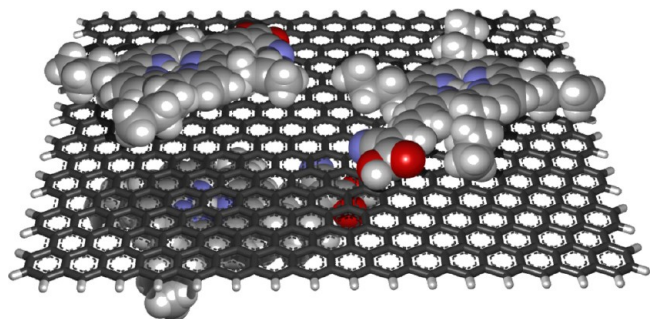
short-lived (i.e., 360 ps) and recombines via charge recombination to reinstate the ground state.

More successful in terms of graphite exfoliation was the use of an amphiphilic pyrene derivative, namely trimethyl-(2-oxo-2-pyren-1-yl-ethyl)ammonium bromide (pyrene⁺), in water. Owing to the predominant hydrophobic nature of pyrene⁺, it has already been shown to exfoliate SWCNTs with great success.^{10a} No evidence for dark state doping was derived in the case of semiconducting SWCNTs.³⁸ For graphite exfoliation, a slightly modified workup procedure was developed—starting from graphite, exfoliation was performed in water with the help of pyrene⁺, from which π - π and hydrophobic interactions originate; see Scheme 5.³⁹ The formation of stable suspensions of few-layer graphene was shown by AFM and TEM. In addition, Raman investigations verified the efficient exfoliation of graphite into single- and few-layer graphene flakes. The D-band intensified during the exfoliation as a reflection of diminished flake sizes, and the 2D-band red-shifts and transforms into a highly symmetric peak at 2675 cm⁻¹. Exemplarily, it was best-fit by four Lorentzians, which is indicative for bilayer graphene, reflecting the highly exfoliated character of the natural graphite crystals. As to the nature of pyrene⁺, fluorescence measurements confirmed the immobilization of individualized pyrene⁺. The resulting bilayer graphene/pyrene⁺ emerged as a versatile platform to graft negatively charged building blocks in water. Initial assays focused on porphyrins (i.e., zinc-5,15-bis(4'-tert-butyl-2',6'-bis-(2'',2''-biscarboxylethyl)phenyl)-10,20-bis(4'-tert-butylphenyl)porphyrin octasodium salt)—porphyrin⁻—later followed by nanocrystals—*vide infra*. Notably, the bulky substituents placed at the

meso-position of the porphyrin macrocycle hampered direct electronic interactions with, for example, the basal plane of graphene. As a matter of fact, the interactions are driven almost exclusively by Coulomb forces—proven by reference experiments, in which the use of positively charged porphyrins (i.e., zinc 5,10,15,20-tetrakis-(2',6'-bis-(*N*-methylene-(4''-tert-butylpyridinium))-4'-tert-butylphenyl) porphyrin octabromide)—porphyrin⁺—indicated no appreciable interactions. Nevertheless, pyrene⁺ turned out to be a potent mediator of, for example, electron transfer between porphyrin⁻ in the excited state and bilayer graphene. The net result of such an electronic interaction is a metastable charge transfer state—150 ps. On one hand, the excited state electron donating porphyrin⁻ is oxidized, as verified through monitoring the respective fingerprint of the π -radical cation. On the other hand, the negative charge has been injected into bilayer graphene. In this context, we have noticed that within ca. 15 ps the bilayer graphene related bleaching in the near-infrared transforms into a positive absorption with a maximum at 1100 nm.

As this approach is limited by the prior exfoliation with a cationic pyrene⁺, direct exfoliation came from using a porphyrin – 5,10,15,20-tetrabutyl-2-(4'-carboxy-4'-cyano-buta-1',3'-dien-1-yl)porphyrin (amphiphilic porphyrin); see Scheme 6.⁴⁰ Importantly, the hydrophobic part of the porphyrin is the key toward successful exfoliation of graphite to yield stable suspensions of single-layer graphene, as confirmed by comprehensive Raman, AFM, and TEM assays. For instance, nonresonant Raman experiments (i.e., 1064 nm) reveal a symmetric 2D-band, with a 2D/G ratio of around

SCHEME 6. Schematic Representation of Noncovalently Functionalized Graphene (i.e., single-layer graphene) by Means of an Amphiphilic Porphyrin (amphiphilic porphyrin)



amphiphilic porphyrin

1 and a fwhm of 53 cm^{-1} when fit by a single Lorentzian; Figure 2. In addition, chemical doping by shifting electron density from the electron donating amphiphilic porphyrin to single-layer graphene is a consequence of mutually interacting constituents, which dominates the ground and excited state characteristics. Owing to the tied electronic coupling of the porphyrin to the basal plane of single-layer graphene, resonant Raman experiments (i.e., 633 nm) enabled recording the porphyrin characteristics. Moreover, the photoexcited but quenched state of amphiphilic porphyrin is the inception of the formation of a 265 ps lived charge transfer state. In the visible, distinct minima at 620 nm as well as maxima at 860 nm confirmed the presence of the porphyrin π -radical cation. In the near-infrared, which is immediately after photoexcitation dominated by a bleaching, new features were noted during the transient decay. Most notable are the minima at 970 nm.

The hydrophilic part of the porphyrin revealed another benefit, that is, being a powerful anchor for grafting TiO_2 nanoparticles. From TEM images the important conclusion is derived that when TiO_2 nanoparticles were added, their presence is restricted to surface areas of single-layer graphene/amphiphilic porphyrin (Figure 3).

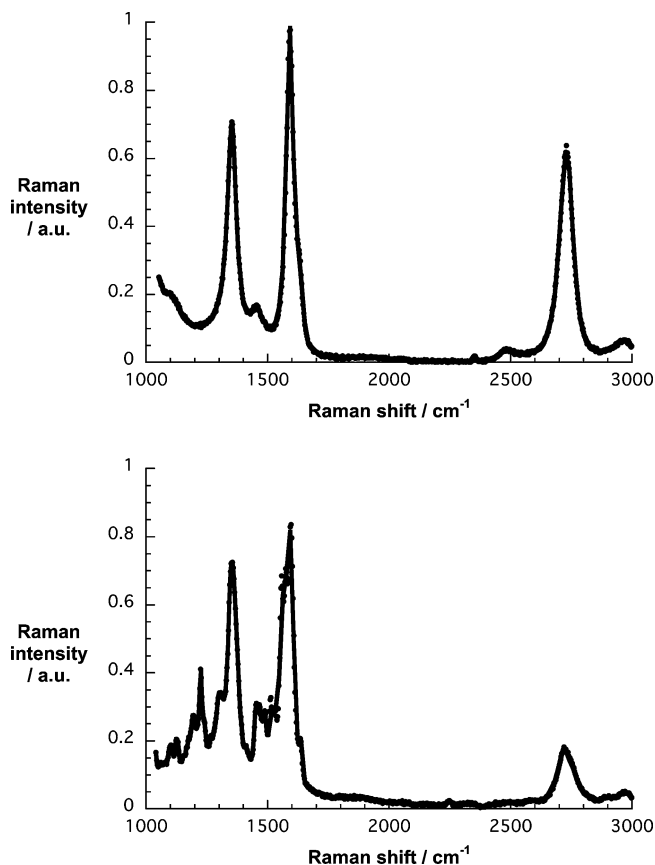


FIGURE 2. (Upper part) Raman spectrum of a single-layer graphene/amphiphilic porphyrin dispersion in THF drop-cast onto a silicon oxide wafer and excited at 1064 nm. (Lower part) Raman spectrum of a single-layer/amphiphilic porphyrin dispersion in THF drop-cast onto a silicon oxide wafer and excited at 633 nm.

Noncovalent Approaches To Immobilize Particulate Building Blocks onto Graphene

In an alternative approach, we pursued the use of CdTe quantum dots (QDs), whose superior tunability in terms of chemical, optical, and electronic properties is a key asset as a unique light harvester in solar cells and as remarkable electron donors.³⁸ In particular, the integration of QDs onto the basal plane of graphene was possible via π - π -interacting pyrene, which was covalently linked to QDs—CdTe QD-pyrene; see Scheme 7.⁴¹ Spectroscopic and microscopic investigations indicate that exfoliation is, however, far from quantitative.⁴² In comparison to the case of pristine graphite, we reach the conclusion that we are dealing with multilayer graphene—exfoliated graphite—rather than graphene. In fact, the coexistence of few-layer and multilayer graphene is, for example, discernible in HRTEM and TEM with flake sizes from 0.27 nm^2 up to 12.7 nm^2 , on which the QDs are immobilized. The photophysical investigation with particular emphasis on the electronic communication

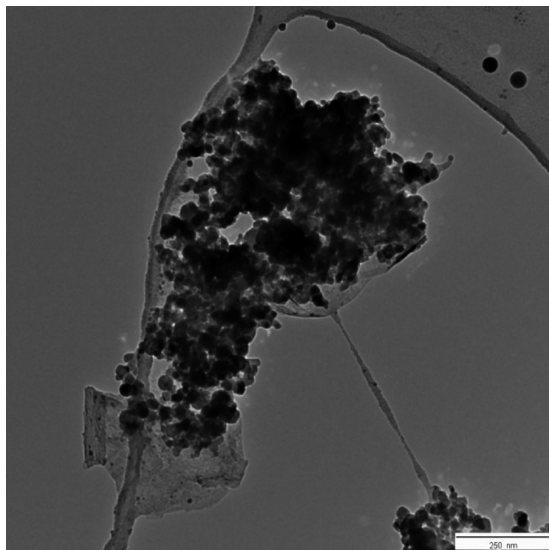


FIGURE 3. TEM image of a single-layer graphene/amphiphilic porphyrin dispersion with TiO_2 in THF drop-cast onto lacey carbon grids.

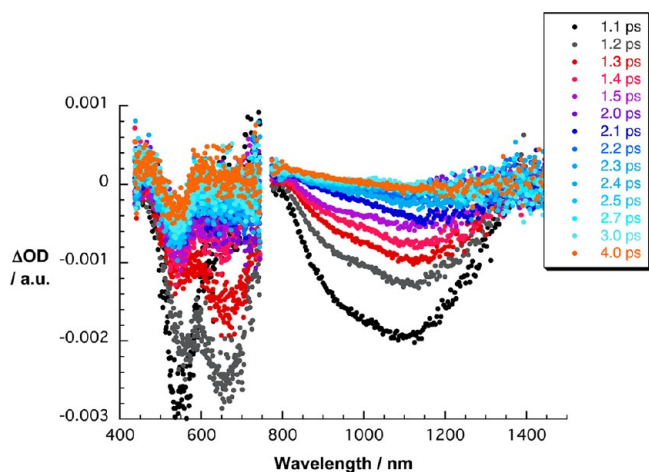
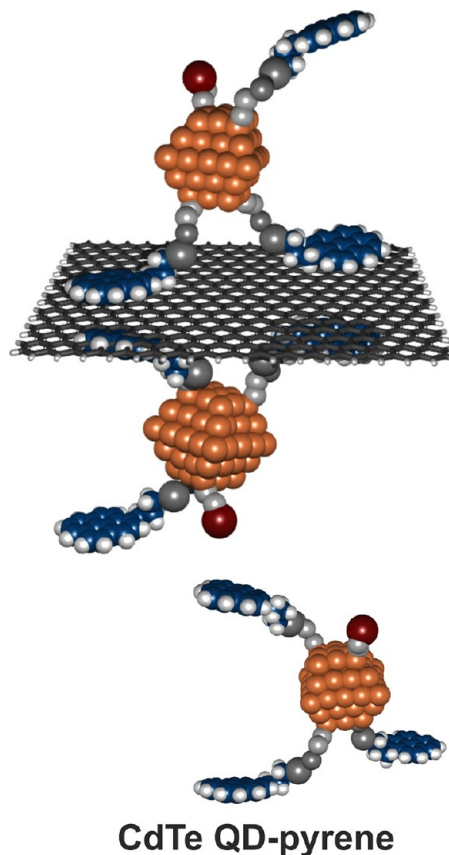


FIGURE 4. Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (387 nm) of $\text{CdTe QD}^-/\text{pyrene}^+/\text{bilayer graphene}$ in water with several time delays between 1.1 and 4.0 ps at room temperature.

between CdTe QD-pyrene and exfoliated graphite highlights that the rather poor degree of exfoliation exerts a negative impact on the efficiency of the electronic communication. Nevertheless, in time-resolved transient absorption measurements by means of pump probe experiments, lifetime reductions of the processes (i.e., filling of shallow and deep traps, etc.) after excitation of QDs by approximately 40% occur due to interactions with the graphenoid material.

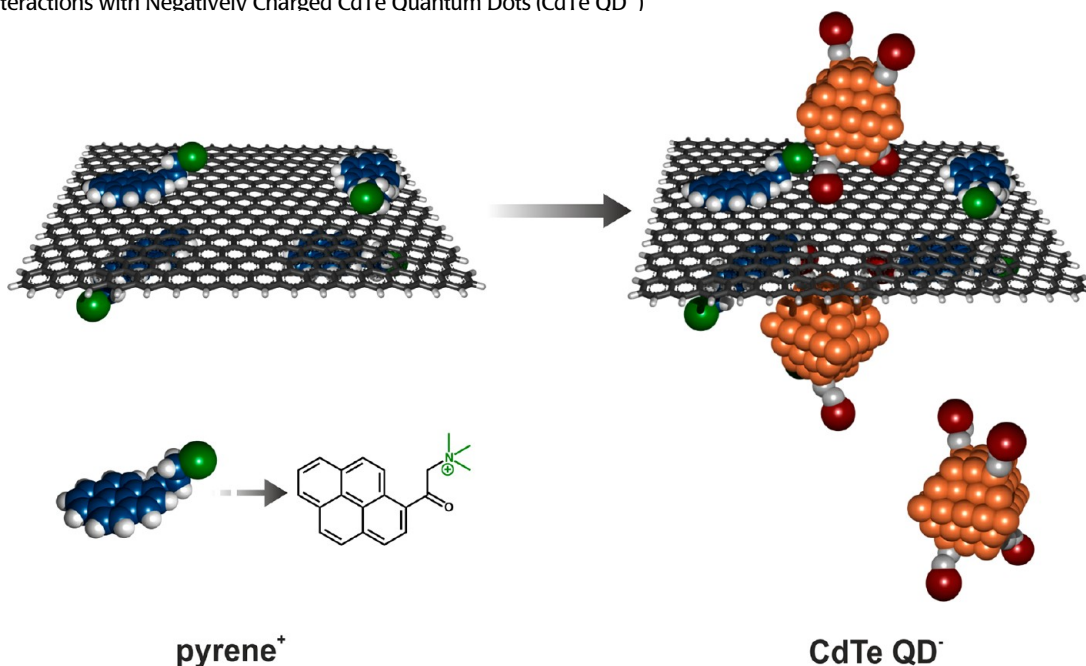
More successful was the approach to prepare *a priori* stable dispersions in water of bilayer graphene by a wet chemical approach. Here, the aforementioned workup of

SCHEME 7. Schematic Representation of Noncovalently Functionalized Graphene (i.e., exfoliated graphite) by Means of Pyrene Linked CdTe Quantum Dots (CdTe QD-pyrene)



graphite with pyrene^+ offers the incentive of $\pi-\pi$ and hydrophobic interactions—*vide supra*. The resulting bilayer graphene was then electrostatically linked to water-soluble QDs that were stabilized with thioglycolic acid; see Scheme 8. As a matter of fact, hierarchical structures were realized that are composed of exfoliated bilayer graphene, positively charged pyrene^+ , and negatively charged QDs— CdTe QD^- . Complementary microscopic assays reveal that the QDs are quantitatively immobilized onto the basal plane of graphene. Furthermore, detailed photophysical characterizations support the notion that from excitonic states of QDs—next to filling of deep and shallow traps—a fast electron transfer evolves to bilayer graphene on the picosecond time scale (Figure 4). In particular, the QD centered transient, on one hand, transforms into a new maximum at 750 as a reflection of QD oxidation. The bilayer graphene centered bleaching, on the other hand, red-shifts from 1120 to 1220 nm, indicating reduced bilayer graphene. Interesting is the fact that GO and few-layer graphene under similar conditions lack such features due to lattice

SCHEME 8. Schematic Representation of Noncovalently Functionalized Graphene (i.e., bilayer graphene) by Means of Pyrene⁺ Followed by Electrostatic Interactions with Negatively Charged CdTe Quantum Dots (CdTe QD⁻)

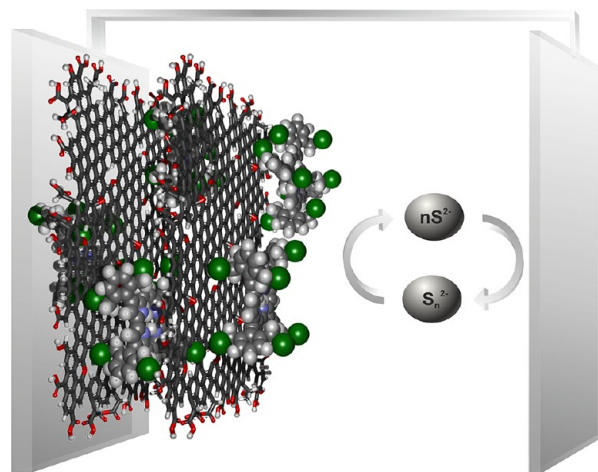


defects/dopants that impact phonon mobility and electronic transitions—*vide supra*. The correspondingly formed charge transfer state is metastable and decays with a lifetime of 164 ps.

Graphene Oxide Based Solar Energy Conversion Devices

In light of the electrostatic interactions between GO and porphycene⁺—*vide supra*—they were immobilized by means of layer-by-layer (LbL) deposition onto ITO electrodes to afford novel solar energy conversion devices.³⁵ Two types of photoelectrodes were fabricated. On one hand, a base layer of poly(diallyl-dimethylammonium) (PDDA) was initially deposited onto hydrophobic ITO (i.e., step 1), resulting in positively charged surfaces. The charged nature of the modified ITO electrodes promotes the deposition of negatively charged GO (i.e., step 2). The resulting ITO/PDDA/GO electrodes were immersed in an aqueous solution of porphycene⁺ (i.e., step 3) to afford ITO/PDDA/GO/porphycene⁺ (Scheme 9). Sequentially repeating steps 2 and 3 led to (GO/porphycene⁺) stacks and, in turn, to ITO/PDDA/(GO/porphycene⁺)_n. On the other hand, deposition of a poly(sodium-4-styrenesulfonato) (PSS) layer onto ITO/PDDA (i.e., step 2) was conducted prior to depositing either GO or porphycene⁺. With the surfaces sufficiently overlaid with negative charges, porphycene⁺ (i.e., step 3) was deposited onto ITO/PDDA/PSS. After this step, a GO layer (i.e., step 4)

SCHEME 9. Schematic Representation of the Integration of Noncovalently Functionalized GO and Porphycene⁺ onto ITO/PDDA Modified Electrodes in the Form of (GO/Porphycene⁺)



was deposited on top of porphycene⁺ as described above. The sequential deposition of GO and porphycene⁺, that is, repeating steps 3 and 4, enabled the successful integration of (GO/porphycene⁺) stacks to yield ITO/PDDA/PSS/(porphycene⁺/GO)_n.

Of importance is that the ITO/PDDA/(GO/porphycene⁺)_n performance enhances as a function of the number of (GO/porphycene⁺) stacks under reverse bias. Here, the modified photoelectrodes act as cathodes. In contrast, under forward bias, where the modified photoelectrodes function as

anodes, the performance decreases upon increasing the number of (GO/porphycene⁺) stacks. Such a trend relates to different thermodynamic scenarios that are operative under the two polarization schemes. Please note that GO and porphycene⁺ function as electron donor and electron acceptor, respectively. Under reverse bias the electrons flow from ITO via GO and porphycene⁺ to the electrolyte. Increasing the number of (GO/porphycene⁺) stacks enhances the light harvesting without, however, affecting the electron transport process. We note an increase until the deposition of the tenth (GO/porphycene⁺) stack when the performance reaches its maximum. It is notable that, under forward bias, the electron transfer occurs from GO to either porphycene⁺ or ITO. Although the general light harvesting is improved, the electron transport process is disrupted at higher numbers of (GO/porphycene⁺) stacks. Hence, increasing the number of (GO/porphycene⁺) stacks evokes an overall drop of the device performance. The same relationships were observed for ITO/PDDA/PSS/(porphycene⁺/GO)_n. The best device performance included a short-circuit current of 120 μA/cm², a fill factor of 34%, and an efficiency of 4.3 × 10⁻³ %. In this context, the low open-circuit voltage of 0.15 V, as is typically observed for such a type of device, constitutes a limitation.

Graphene Based Solar Energy Conversion Devices

For testing the processability of bilayer graphene that has been exfoliated and stabilized with pyrene⁺ together with the aforementioned porphyrin⁻—*vide supra*—we turned to their assembly onto quartz as well as onto ITO.³⁹ First, bilayer graphene/pyrene⁺ was deposited onto quartz or ITO, which was activated by potassium hydroxide, by immersing in a LbL fashion. AFM analysis reveals a homogeneous coverage of bilayer graphene with a height of maximal 5 nm for the single flakes. Nevertheless, the sheets are folded, packed, and somehow wrinkled. Seemingly only bilayer flakes tend to assemble onto the surface as based on AFM and Raman analyses. Interestingly, the transmittance of a single deposited layer at 550 nm amounted to around 90%. Second, porphyrin⁻ was immobilized. The deposition process was successfully repeated up to seven times, resulting in sandwich layers with bands at 270 and 434 nm that grow linearly with increasing number of layers. The sandwich layers on ITO successfully responded to white light illumination. In particular, with a sodium ascorbate/Na₃PO₄ solution a reproducible and stable photocurrent response of around 360 nA was established in several illumination/dark cycles.

Conclusions and Outlook

The chemistry of graphene, especially the wet chemistry of it, is still in its infancy. Nevertheless, it is currently one of the most promising and fastest developing areas in nanotechnology. To this date, several methodologies en-route toward the chemical manipulation of graphene have been established. Most notable here are the covalent and noncovalent means to realize novel and multifunctional graphene materials. Future developments in this field are easily conceivable, in particular with respect to emerging fields in the sector of electronics reaching from quantum computing and optics to photoconversion systems. In this regard, full control over the attachment of photo- and/or redoxactive building blocks to the basal plane of graphene is, however, imperative. Direct interactions and functionalization upon exfoliation meet this necessity and constitute a fast and scalable approach. Moreover, they open the possibility for the integration and immobilization onto multifunctional surfaces including transparent photoelectrodes, etc. Overall, fine-tuning electron transfer reactions and, in turn, boosting the efficiency of the next generation of solar panels might soon become a reality.

BIOGRAPHICAL INFORMATION

Jenny Malig received her B.Sc. degree in molecular science from the University of Erlangen-Nürnberg, Germany, in 2007 on covalent derivatization of single-walled carbon nanotubes. She finished her M.Sc. in molecular nanoscience in 2009 on synthesis and characterization of porphyrins. As a fellow of the graduate School Molecular Science (GSMS) within the framework of the initiative for excellence of the Bavarian Federal Government, she is currently working as a researcher at the University of Erlangen-Nürnberg as a Ph.D. candidate on functionalization, synthesis, and characterization of graphenoid systems since 2009. She may be reached at jenny.malig@chemie.uni-erlangen.de.

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Dirk M. Guldi is one of the world-leading scientists in the field of charge transfer/nanocarbons. In particular, he is well-known for his contributions to the areas of charge-separation in donor–acceptor

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FOOTNOTES

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