β-Cyclodextrin Encapsulated Coumarin 6 on Graphene Oxide Nanosheets: Impact on Ground-State Electron Transfer and Excited-State Energy Transfer

Rajashree Banerjee,† Riya Sinha,† and Pradipta Purkayastha*†‡

1Department of Chemical Sciences and 4Center for Advanced Functional Materials, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur 741246, West Bengal, India

ABSTRACT: We report a unique phenomenon of physical adsorption of coumarin 6-β-cyclodextrin (C6-β-CD) inclusion nanostructures on graphene oxide (GO) nanosheets, thus inducing ground-state electron transfer from the C6-β-CD composite to GO. On excitation, the C6-β-CD composite initially transfers energy to the attached GO surface and subsequently collides with similar C6-β-CD@GO adducts leading to dynamic quenching of energy. The ground-state two-electron transfer process has been confirmed by cyclic voltammetry in aqueous medium, whereas the excited-state processes were inferred from steady-state and time-resolved fluorescence spectroscopy. The concept is developed toward conceiving control over the ground-state electron transfer and excited state energy transfer from the C6-β-CD composite by the adsorbed electron accepting medium (GO in this case). The C6-β-CD composite has been prepared to isolate single C6 molecules that readily undergo microcrystal formation in aqueous medium. The results show its potential toward fabrication of energy-harvesting antenna for further applications.

INTRODUCTION

Graphene, an extremely well-studied carbon material, is known for its unusual magnetic, electronic, optical, and thermal properties.1–5 It also shows potential to be a useful material for solar-energy-conversion and low-cost optoelectronic devices.6–8 Graphene can be chemically or thermally synthesized from graphite oxide (GO),11–13 GO, on the other hand, is prepared by chemically oxidizing graphite followed by dispersion and exfoliation in a suitable solvent.14 GO mostly contains hydroxyl and epoxy functional groups on the basal plane, and carboxyl, carbonyl, phenol, lactone, and quinone in small amounts at the edges of the sheet.15–17 The oxygen-containing functional groups in GO strongly affect the inherent electronic and electrochemical properties, which distinguish it from graphene.18 Moreover, the polarities of the oxygen-containing functional groups make GO a strongly hydrophilic one exhibiting good dispersive property in many organic solvents including water.19,20 GO contributes in preparing excellent electrode material by immobilizing various electroactive species using the surface functionalities.15,21 Electrochemical applications of GO-based materials have become extensively popular nowadays. These devices are cost effective in context to the preparation of thin layers on conventional electrodes as only a fraction of these materials is required in this process.

Structurally, GO is different from pristine graphene that consists only of trigonally bonded sp² carbon atoms.22 The GO sheet consists mostly of a hexagonal ring-based carbon system bearing sp² carbon atoms and also (partly) sp³ carbons which bear the oxygen-containing functional groups.23 The structural peculiarity has enabled GO to accept electrons from dedicated donors. The electron-accepting ability of GO, specifically reduced GO (rGO), has been much exploited in the area of photocatalysis where shuffling of electrons between the rGO host and various guests has been effectively used.24–28 In many cases enhancement in charge transport property could be achieved using TiO₂–rGO nanocomposites.24–27 Furthermore, a study on the effect of temperature on electron transfer from a freely interacting dye to an rGO nanosheet is also reported.28 GO can be decorated with electron donor and electron acceptor compounds for photoinduced electron transfer (PET) procedure. Das et al. used this technique by covalently linking the donor and acceptor molecules to the GO sheet.29 In applications on metal oxide/poly(3-hexylthiophene) hybrid solar cells, it has been shown that rGOS enhance the charge separation.30 Recently, we have been working with a well-known laser dye, Coumarin 6 (C6) (Figure 1). This dye is special in the coumarin family as it contains a benzothiazole ring with the parent moiety, which imparts donor–acceptor character to the compound. The fluorescence quantum yield of such coumarin derivatives are reportedly low in polar solvents due to the transformation of the fluorescent intramolecular charge transfer (ICT) state to the non-emissive twisted ICT state.31 However, the characteristics of C6 are even special because a new red-shifted absorption band is observed for this

Received: July 25, 2019
Accepted: September 6, 2019
Published: September 19, 2019
compound at 500 nm in an aqueous medium with time along with its original absorption peaking at 460 nm. The emission spectrum of C6 also shows an additional shoulder at 550 nm along with the normal fluorescence band at 530 nm upon exciting the compound at 430 nm. This extra band has been explained to form due to microcrystallization of C6 in water. The microcrystal formation of C6 was reported long back by Fery-Forgues et al., which they obtained from reprecipitation method and at a very high concentration of the dye. However, we found the C6 microcrystals formed even at a much lower concentration (~1 μM) than what reported at room temperature in aqueous environment. This process considerably lowers the fluorescence yield of C6 with time. In a series of studies, we have shown several ways to revive the lost fluorescence of C6 in water by using various hosts that have relatively hydrophobic cavities. Using biocompatible hosts, such as, β-cyclodextrin (β-CD), micelles, proteins, and single-walled carbon nanotubes, the microcrystalline states of C6 could be broken and the fluorescence emission could be revived. This technique could be successfully applied in energy transfer reactions in the excited state.

It has been shown that the rate of excited state electron transfer is much faster compared to that of the ground-state phenomenon because of the proximity and the resonance factors. Thus, adsorption of a guest system to a host, either physically or chemically, is likely to undergo such consequences. It has also been shown that ground-state charge transfer depends on proper alignment in ionization potential or electron affinity. Theoretical studies on π-π complexes have revealed that the extent of ground-state charge transfer depends on the substitution of the donor that determines the donatability or acceptability of electrons. The present work does not merely demonstrate PET from dye to GO, but add a dual conception. Using the above descriptions on electron transfer in the ground and the excited states, we have exploited one of the methods to revive C6 fluorescence in water using β-CD encapsulation combining with the electron accepting property of GO to devise a simple process of ground-state electron transfer and excited state energy transfer. C6 and β-CD form planar and strongly fluorescent nanoaggregates by guest–host chemistry. The π-π stacking ability of C6 has been used in physical adsorption (physisorption) of the C6-β-CD composites on the GO surface. The electron/energy donatability of the coumarin dye could be suitably modulated by GO using this process. Energy transfer from coumarin to an acceptor has been reported previously using reverse micelles and covalently bonded β-CD, but the approach reported herein is completely new and has huge potential to be used in energy harvesting as the observations are based on π-π interactions and noncovalent exchange.

**RESULTS AND DISCUSSION**

**Spectral Characteristics.** The absorption spectrum of C6 shows the characteristic peaks at 460 and 500 nm, the former is for the C6 molecule and the latter for the microcrystal formed due to aggregation (Figure 2). On the addition of 7 mM β-CD to the aqueous C6 solution (having 1% ethanol as cosolvent), the absorbance increased considerably at 460 nm along with the disappearance of the band at 500 nm. This signifies disintegration of the C6 microcrystals by the hydrophobic β-CD cavities and consequently encapsulating the single C6 molecules. This behavior of C6 in water and β-CD has been reported and explained earlier by us in detail. Interestingly, the absorbance decreases on gradual addition of GO. The results indicate profuse interaction of the C6-β-CD composites with the GO sheets. We mention the C6 and β-CD complex as “C6-β-CD composites” as the product does not have a simple 1:1 or 1:2 guest–host stoichiometry, but a nanostructure formed by self-accumulation of the individual 1:2 C6-β-CD through hydrogen bonding at the outer rims of the CDs.

Figure 2 shows that on the addition of GO to the C6-β-CD composite, the absorbance decreases and saturates after adding 16 μg/mL of GO to the solution where the absorption spectrum remained practically unchanged on further addition of GO. Subsequently, the fluorescence spectra were collected by exciting the samples at 430 nm (Figure 3). The fluorescence yield of C6 in water decreased considerably with time due to the microcrystal formation because of aggregation of the C6 molecules. The emission spectrum is structurally broad...
with a shoulder at 550 nm along with the main fluorescence band at 530 nm. Application of 7 mM β-CD enhanced the fluorescence yield considerably with the disappearance of the band at 550 nm, indicating the revival of the lost C6 fluorescence. This has been found to be due to disintegration of the C6 microcrystals to liberate the C6 molecules which are encapsulated by the β-CD hosts.32 As reported earlier, these guest–host complexes are 1:2 in nature and the individual composites aggregate through hydrogen bonding between the hydroxyl groups located at the periphery of β-CDs. The consequence is the formation of planar, square, and green fluorescence nanostructures in solution.32 Addition of GO gradually quenches the fluorescence from the C6-β-CD nanostructures without any shift in the emission maximum or broadening of the emission spectrum. Thus, it can be presumed that the interaction has not destroyed the C6-β-CD nanostructures to release C6 into the polar aqueous bulk, but quenched the emission from the nanostructures through a different mechanism.

**Analysis of the Quenching of C6 Fluorescence.** The Stern–Volmer plots of the quenched fluorescence data provided interesting observations (Figure 4). The $F_0/F$ plot against the concentration of GO was clearly bimodal. The initial part deviated upward from linearity up to 16 μg/mL of GO and subsequently straightened to become perfectly linear. The concept of the Stern–Volmer quenching plot reveals that upward deviation from linearity indicates a combination of static and dynamic quenching, whereas no such deviation indicates the occurrence of only one type of quenching.33 The indications matched quite well with the absorption spectra (Figure 2), where we observed change in the spectrum up to an addition of 16 μg/mL of GO to C6-β-CD in water followed by a practically unchanged spectrum. This shows that the species had initially suffered a static quenching due to the formation of ground-state composites. The nonlinear Stern–Volmer plot shows dynamic quenching of energy of the C6-β-CD@GO composites in the excited state. The linearity appears at higher GO concentration (beyond 20 μg/mL) due to collisional (pure dynamic) quenching between the C6-β-CD@GO composites. This could happen, presumably, because the adsorption of the β-CD-C6 composites over the GO nanosheets becomes saturated, hence plenty of C6-β-CD@GO composites become available for free collision and hence execute dynamic quenching of fluorescence.

**Time-Resolved Fluorescence Decay Studies.** The time-resolved emission decay studies further confirmed our hypothesis (Figure 5). The samples were excited using a 405 nm diode laser which mostly excites the C6 monomers. Table 1 summarizes the results obtained by fitting the raw data acquired from the different emitting species. In each case, the data took a two-component exponential decay fit. For blank C6 in water, the slower component ($τ_i$) indicates emission lifetime of the locally excited C6 molecule and the faster one ($τ_2$) shows that of the aggregate.32,35 On addition of β-CD, we obtained a fast growth component ($τ_1$) (signified by the negative percentage contribution) indicating the time scale of residence of the excited species for ICT for the β-CD-encapsulated C6 due to 1:2 guest–host binding.32,35 On progressive addition of GO (4–14 μg/mL as per Table 1), we noticed subsequent lowering of the growth component which, probably, shows that the reduction in ICT might be because of the ground-state electron transfer process as the C6-β-CD nanostructures get adsorbed over the GO nanosheets (as schematically modeled in Scheme 1 later). On further increasing the GO concentration, an extremely fast decay component shares the major contribution (shown in italics in Table 1). Because a 405 nm diode laser was used to excite the samples and as its temporal resolution is <200 ps, we do not

---

**Figure 4.** The Stern–Volmer quenching plot derived from the emission spectra of C6 in β-CD with the addition of GO up to 16 μg/mL. The inset shows a similar quenching plot on the subsequent addition of GO up to 50 μg/mL. The Stern–Volmer equation: $F_0/F = 1 + K_{SV}[Q]$ has been used in the plots, where $F_0$ and $F$ are the emission maxima (500 nm) for C6-β-CD without and with GO, respectively, $F_i$ (inset) denotes emission from C6-β-CD added with 20 μg/mL of GO. $K_{SV}$ is the Stern–Volmer constant and Q is the quencher (GO in this case).

| emitting species | $τ_1$ (ps) | $τ_2$ (ns) | $χ^2$ |
|------------------|-----------|-----------|-------|
| C6 (blank)       | 797 (27)  | 2.55 (73) | 1.34  |
| C6-7 mM β-CD     | 623 (−8)  | 2.09 (108)| 1.02  |
| added with       |           |           |       |
| 4 μg/mL GO       | 550 (−6)  | 2.16 (106)| 1.01  |
| 8 μg/mL GO       | 536 (−4)  | 2.25 (104)| 1.07  |
| 14 μg/mL GO      | 669 (−1)  | 2.45 (101)| 1.21  |
| 20 μg/mL GO      | 1.96 (64) | 2.4 (36)  | 1.12  |
| 28 μg/mL GO      | 2.64 (62) | 2.53 (38) | 1.14  |

Note: The $χ^2$ values represent the fitting perfection and the values in parentheses represent the contributions of each of the emitting components. The excitation wavelength is 405 nm. The raw data obtained contain ±5% experimental error.
claim the authenticity of the magnitudes of the ultrafast times which are shown in italics in Table 1. However, the information on the ultrafast decay is sufficient to analyze the results (Figure 5). The ultrafast decay components can well be argued to appear because of the dynamic collisions between the C6-β-CD@GO composites as observed in the steady-state quenching studies before. Using an appropriate filter to eliminate the scattering signals (if any) at higher GO concentration leads us to this conclusion.

Mechanistic Details. Generally, absorption of light by a species reduces on decrease in their free existence. Hence, it is understandable that the amount of free C6-β-CD nanostructures was reduced in the presence of GO. The results indicate a possible interaction of the C6-β-CD nanostructures with the added GO. To investigate the nature of interaction between the two species, their individual structural characteristics could be excavated. C6 has stacking propensity through π-π interaction as observed before from their tendency to form microcrystals. The N,N′-dialkyl substituted coumarin derivatives favor ICT due to their planar forms that develop partially charged separated ground-state species. This increases the possibility of development of parallel stacks through van der Waals as well as electrostatic interactions. However, in the present case, the presence of β-CD in solution imposes disintegration of the C6 microcrystals and encapsulation of the fluorophores inside the β-CD cavity. The process produces planar and square nanostructures as mentioned before and hence revives the ICT to regain the fluorescence emission.

Scheme 1 provides a diagrammatic representation of the hypothesis. Quenching of C6-β-CD fluorescence in the presence of GO is clearly visualized in epifluorescence microscopy images (Figure 6).

Cyclic Voltammetry To Prove the Electron Transfer Process. The above description on the static and dynamic quenching of the nanocomposites is evident from the spectroscopic findings. However, the ground-state electron transfer process needs to be proven experimentally. The ICT in C6 molecules trapped in β-CD is suppressed due to adsorption of the C6-β-CD nanocomposites on the GO nanosheets as hypothesized due to intermolecular electron transfer from C6 to GO which is a good electron acceptor as well as conductor. The process demands two-electron transfer because there is a lone pair of electrons over the N-atom in the N,N-diethylamine group in C6. To prove this, we performed cyclic voltammetry (CV) with C6 under the various conditions as described in the text. The voltammograms obtained are provided in Figure 7.

The CV experiment was performed at three different scan rates, viz., 50, 75, and 100 mV/s. The plot of the anodic peak current versus the square root of the scan rate is linear (Figure 8). Moreover, the peak voltage remained fixed at 0.72 V for all the three different scan rates. Thus, the overall electron transfer process is diffusion controlled and reversible in nature. The two oxidation peaks are due to the two-electron transfer phenomenon. The electrochemical reversibility describes the rate of electron transfer. The signals indicate that the electron...
transfer becomes much easier when C6 is encapsulated in the β-CDs and adsorbed on the surface of the GO nanosheets. It was observed that the first oxidation peak arises at a lower potential for C6-β-CD@GO (57 mV) compared to C6-β-CD (123 mV). Hence, oxidation (loss of electron of C6 to GO) becomes easier in the presence of the GO nanosheets in an aqueous medium. The experimental evidence clearly states that the electron over the N-atom of the N,N-diethylamine group in C6 that was participating in ICT when encapsulated in the β-CDs later moves to GO through an intermolecular electron transfer. The process was not prominent between the C6 microcrystals and the GO nanosheets, but pronounced as β-CDs disintegrated the nanocrystals and encapsulated the C6 molecules.

CONCLUSIONS

A unique process of disintegration of self-assembled C6 molecules by β-CDs, thus, reviving the lost fluorescence of a laser dye followed by physical adsorption on GO nanosheets and inducing ground-state electron transfer from the C6-β-CD composite to GO, has been experimentally illustrated. On excitation, the C6-β-CD composite initially transfers energy to the attached GO surface and subsequently when the GO surface gets saturated with the adsorbed C6, the emitting composites collide with excess GO and results into dynamic quenching of energy. Electrochemistry confirms the ground-state two-electron transfer process. The results show that the ground-state electron transfer and excited state energy transfer from the C6-β-CD composite can be controlled by adding GO which is a good electron acceptor. The findings have the potential toward fabrication of energy-harvesting antenna for further applications.

EXPERIMENTAL SECTION

Materials. C6, β-CD (purity > 97%), and 4–10% edge-oxidized GO (EOGO or GO) were purchased from Sigma-Aldrich and used as received. HPLC grade water was used throughout the experiment. A 50 μL of stock solution (50 μM) of C6 in methanol was added to water to get its final concentration as 1 μM. β-CD (0.0199 g) was added to the experimental solution to get the final concentration as 7 mM. This concentration of β-CD was used following our previous observations to ensure encapsulation of most of the C6 molecules. A stock solution of GO (1 mg/mL) was prepared in water by sonication and added to the experimental solution in steps for the various studies.

Methods. The absorption and fluorescence spectra were collected by using a Hitachi U-2900 spectrophotometer and a PTI QM-40 spectrofluorimeter. The fluorescence lifetimes were measured using a time-correlated single photon counting method in a spectrofluorimeter from Horiba Jobin Yvon IBH equipped with a FC-MCP-50SC MCP-PMT detection unit. The excitation pulse used was 405 nm (temporal resolution < 200 ps). The raw data were fitted using DAC software supplied with the machine. The epifluorescence images were taken using an LSM 710 with a microscope Axio-Observer Z.1 from Carl Zeiss. The CV experiments were done using Newport Oriel Instruments, U.S.A.–69907. The electrochemical measurements were carried out in acidulated water as the electrolyte, Pt as the working electrode, Ag/Ag⁺ as the reference electrode, and Pt wire as the counter electrode with samples (i) C6-β-CD, (ii) C6-7 mM β-CD, (iii) C6-7 mM β-CD-28 μg/mL of GO, and (iv) C6-28 μg/mL of GO. A total of 7.5 mL of solution was placed in a three-necked vessel and the data were plotted at three different scan rates: 50, 75, and 100 mV/s. The anodic peak current against the square root of the scan rate was plotted to ensure the reversible electron transfer process in C6.

AUTHOR INFORMATION

Corresponding Author
*E-mail: ppurkayastha@iiserkol.ac.in.

ORCID
Pradipta Purkayastha: 0000-0001-8825-1207

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work was supported by the Science and Engineering Research Board (SERB), Government of India through the grant CRG/2018/000555, and the Council of Scientific and Industrial Research (CSIR) through the grant 01(2958)/18/EMR-II. R.B. and R.S. gratefully acknowledge IISER Kolkata for their fellowships.

REFERENCES

(1) Matte, H. S. S. R.; Subrahmanyam, K. S.; Rao, C. N. R. Novel Magnetic Properties of Graphene: Presence of Both Ferromagnetic and Antiferromagnetic Features and Other Aspects. J. Phys. Chem. C 2009, 113, 9982–9985.
(2) Jedrzejewska, A.; Kilanski, L.; Libersa, D.; Lewińska, S.; Ślawaska-Wanieńska, A.; Wrobł, P. S.; Bachmatiuk, A.; Jedrzejewski, R. Structural and Magnetic Properties of Graphene-Based Fe₂O₃-Decorated Composites. J. Magn. Magn. Mater. 2019, 471, 321–328.
(3) Nigar, S.; Zhou, Z.; Wang, H.; Imitz, M. Modulating the Electronic and Magnetic Properties of Graphene. RSC Adv. 2017, 7, 51546–51580.
(4) Dedkov, Y. S.; Fonin, M. Electronic and magnetic properties of the graphene-ferromagnet interface. New J. Phys. 2010, 12, 125004.
(5) Falkovsky, L. A. Optical Properties of Graphene. J. Phys.: Conf. Ser. 2008, 129, 012004.
(6) de Weerd, C.; Shin, Y.; Marino, E.; Kim, J.; Lee, H.; Saeed, S.; Gregorčič, T. Comparison of the Optical Properties of Graphene and Alkyl-Terminated Si and Ge Quantum Dots. Sci. Rep. 2017, 7, 14463.
(7) Shahil, K. M. F.; Balandin, A. A. Thermal Properties of Graphene and Multilayer Graphene: Applications in Thermal Interface Materials. Solid State Commun. 2012, 152, 1331–1340.
(8) Pop, E.; Vanherpen, V.; Roy, A. K. Thermal Properties of Graphene: Fundamentals and Applications. MRS Bull. 2012, 37, 1273–1281.
(9) Ahmed, F.; Brajpuria, R. K.; Handa, Y. A Review on Graphene Based Solar Cells. Int. J. Recent Sci. Res. 2017, 8, 16893–16896.
(10) Wang, J.; Ma, F.; Liang, W.; Wang, R.; Sun, M. Optical, Photonic and Optoelectronic Properties of Graphene, h-BN and Their Hybrid Materials. *Nanophotonics* 2017, 6, 943–976.

(11) Ang, P. K.; Wang, S.; Bao, Q.; Thong, J. T. L.; Loh, K. P. High-Throughput Synthesis of Graphene by Intercalation–Exfoliation of Graphite Oxide and Study of Ionic Screening in Graphene Transistor. *ACS Nano* 2009, 3, 3587–3594.

(12) Li, X.; Cai, W.; An, J.; Kim, S.; Nah, J.; Yang, D.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S. Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science* 2009, 324, 1312–1314.

(13) De Arco, L. G.; Zhang, Y.; Schlenker, C. W.; Ryu, K.; Thompson, M. E.; Zhou, C. Continuous, Highly Flexible, and Transparent Graphene Films by Chemical Vapor Deposition for Organic Photovoltaics. *ACS Nano* 2010, 4, 2865–2873.

(14) Dreyer, D. R.; Park, S.; Bielawski, C. W.; Ruoff, R. S. The Chemistry of Graphene Oxide. *Chem. Soc. Rev.* 2010, 39, 228–240.

(15) Eda, G.; Chhowalla, M. Chemically Derived Graphene Oxide: Towards Large-Area Thin-Film Electronics and Optoelectronics. *Adv. Mater.* 2010, 22, 2392–2415.

(16) Li, X.; Zhang, G.; Bai, X.; Sun, X.; Wang, X.; Wang, E.; Dai, H. Highly conducting graphene sheets and Langmuir-Blodgett films. *Nat. Nanotechnol.* 2008, 3, 538–542.

(17) Kim, F.; Cote, L. J.; Huang, J. Graphene Oxide: Surface Activity and Two-Dimensional Assembly. *Adv. Mater.* 2010, 22, 1954–1958.

(18) Gómez-Navarro, C.; Meyer, J. C.; Sundaram, R. S.; Chuvilin, A.; Kurash, S.; Burgard, M.; Kern, K.; Kaiser, U. Atomic Structure of Reduced Graphene Oxide. *Nano Lett.* 2010, 10, 1144–1148.

(19) Paredes, J. I.; Villar-Rodil, S.; Martinez-Alonso, A.; Tascón, J. M. D. Graphene Oxide Dispersions in Organic Solvents. *Langmuir* 2008, 24, 10560–10564.

(20) Compton, O. C.; Nguyen, S. T. Graphene Oxide, Highly Reduced Graphene Oxide, and Graphene: Versatile Building Blocks for Carbon-Based Materials. *Small* 2010, 6, 711–723.

(21) Mattevi, C.; Eda, G.; Agnoli, S.; Miller, S.; Mkhoyan, K. A.; Celik, O.; Mastrogiovanni, D.; Granazzo, G.; Garfunkel, E.; Chhowalla, M. Evolution of Electrical, Chemical, and Structural Properties of Transparent and Conducting Chemically Derived Graphite Thin Films. *Adv. Funct. Mater.* 2009, 19, 2577–2583.

(22) Liu, C. H.; Liu, L.; Mak, K. F.; Flynn, G. W.; Heinz, T. F. Ultraflat Graphene. *Nature* 2009, 462, 339–341.

(23) Szabo, J.; Berkei, O.; Forgó, P.; Josepovits, K.; Sanakis, Y.; Petridis, D.; Dékány, J. Evolution of Surface Functional Groups in a Series of Progressively Oxidized Graphite Oxides. *Chem. Mater.* 2006, 18, 2740–2749.

(24) Zhang, Y.; Tang, Z.-R.; Fu, X.; Xu, Y.-J. TiO2–Graphene Nanocomposites for Gas-Phase Photocatalytic Degradation of Volatile Aromatic Pollutant: Is TiO2–Graphene Truly Different from Other TiO2–Carbon Composite Materials? *ACS Nano* 2010, 4, 7303–7314.

(25) Zhang, H.; Lv, X.; Li, Y.; Wang, Y.; Li, J. P25-Graphene Composite as a High Performance Photocatalyst. *ACS Nano* 2010, 4, 380–386.

(26) Du, J.; Lai, X.; Yang, N.; Zhai, J.; Kisailus, D.; Su, F.; Wang, D.; Jiang, L. Hierarchically Ordered Macro-Mesoporous TiO2–Graphene Composite Films: Improved Mass Transfer, Reduced Charge Recombination, and Their Enhanced Photocatalytic Activities. *ACS Nano* 2011, 5, 590–596.

(27) Gan, Z.; Wu, X.; Meng, M.; Zhu, X.; Yang, L.; Chu, P. K. Photothermal Contribution to Enhanced Photocatalytic Performance of Graphene-Based Nanocomposites. *ACS Nano* 2014, 8, 9304–9310.

(28) Gan, Z.; Guo, J.; Di, Y.; Li, R.; Huang, S. Electron transfer from organic dyes to reduced graphene oxide studied by photoluminescence spectroscopy. *Phys. Status Solidi B* 2016, 253, 1138–1143.

(29) Das, S. K.; KC, C. B.; Okhobo, K.; Yamada, Y.; Fukuzumi, S.; D’Souza, F. Decorating Single Layer Graphene Oxide with Electron Donor and Acceptor Molecules for the Study of Photoinduced Electron Transfer. *Chem. Commun.* 2013, 49, 2013–2015.

(30) Cho, H.-W.; Liao, W.-P.; Lin, W.-H.; Yoshimura, M.; Wu, J.-J. Pristine Reduced Graphene Oxide as an Energy-Matched Auxiliary Electron Acceptor in Nanarchitectural Metal Oxide/Poly(3-Hexylthiophene) Hybrid Solar Cell. *J. Power Sources* 2015, 293, 246–252.

(31) Abdel-Mottaleb, M. S. A.; Antonious, M. S.; Abo Ali, M. M.; Imam, M. S.; El-Sayed, F. M.; El-Sayed, A. M. Photophysics and Dynamics of Coumarin Laser Dyes and their Analytical Implications. *Proc. – Indian Acad. Sci., Chem. Sci.* 1992, 104, 185–196.

(32) Ghosh, P.; Das, T.; Maity, A.; Mondal, S.; Purkayastha, P. Incorporation of Coumarin 6 in Cycloextrins: Microcrystals to Lamellar Composites. *RSC Adv.* 2015, 5, 4214–4218.

(33) Fery-Forgues, S.; El-Ayoubi, R.; Lamère, J.-F. Fluorescent Microcrystals Obtained from Coumarin 6 using the Reprecipitation Method. *J. Fluoresc.* 2008, 18, 619–624.

(34) Corrent, S.; Hahn, P.; Pohlers, G.; Connolly, T. J.; Scaino, J. C.; Fornés, V.; Garcia, H. Intrazelite Photochemistry. 22. Acid–Base Properties of Coumarin 6. Characterization in Solution, the Solid State, and Incorporated into Supramolecular Systems. *J. Phys. Chem. B* 1998, 102, 5852–5858.

(35) Banerjee, R.; Mondal, S.; Purkayastha, P. Revival, enhancement and tuning of fluorescence from Coumarin 6: combination of host–guest chemistry, viscosity and collisional quenching. *RSC Adv.* 2016, 6, 105347–105349.

(36) Banerjee, R.; Purkayastha, P. Piecemeal Rekindling of Coumarin 6 Fluorescence on Stepwise Unfolding of Protein by Surfactant. *J. Phys. Chem. B* 2017, 121, 11449–11454.

(37) Banerjee, R.; Purkayastha, P. Interaction of Coumarin 6 with Carbon Nanotubes: Disintegration of the Microcrystalline State by Surfactant Aggregation on the Nanotube Surface. *J. Mol. Liq.* 2018, 271, 397–402.

(38) Brennan, J. L.; Howlett, M.; Forster, R. J. Ground vs Excited State Electron Transfer: Adsorbed Monolayers and Trimmers in Solution. *Faraday Discuss.* 2002, 121, 391–403.

(39) Zhang, Q.; Liu, X.; Jiao, F.; Braun, S.; Jafari, M. J.; Crispin, X.; Ederth, T.; Fahlan, M. Ground-State Charge Transfer for NIR Absorption with Donor/Acceptor Molecules: Interactions Mediated via Electrophotogenic and Orbital Symmetries. *J. Mater. Chem. C* 2017, 5, 275–281.

(40) Winget, P.; Brédas, J.-L. Ground-State Electronic Structure in Charge-Transfer Complexes Based on Carbazole and Diarylamine Donors. *J. Phys. Chem. C* 2011, 115, 10823–10835.

(41) Seth, C.; Chakrabarty, D.; Chakraborty, A.; Sarkar, N. Study of Energy Transfer from 7-Amino Coumarin Donors to Rhodamine 6G Acceptor in Non-Aqueous Reverse Micelles. *Chem. Phys. Lett.* 2005, 401, 546–552.

(42) Takakusa, H.; Kikuchi, K.; Urano, Y.; Higuchi, T.; Nagano, T. Intramolecular Fluorescence Resonance Energy Transfer System with Coumarin Donor Included in β-Cycodextrin. *Anal. Chem.* 2001, 73, 939–942.

(43) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 3rd ed.; Springer, 2006.

(44) Jasinski, J. P.; Paigh, E. S. 3-(2-Benzothiazolyl)-7-(diethylamino)coumarin. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 1995, 51, 531–533.