Designing Cascades of Electron Transfer Processes in Multicomponent Graphene Conjugates

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Abstract: A novel family of nanocarbon-based materials was designed, synthesized, and probed within the context of charge-transfer cascades. We integrated electron-donating ferrocenes with light-harvesting/electron-donating (metal)porphyrins and electron-accepting graphene nanoplates (GNP) into multicomponent conjugates. To control the rate of charge flow between the individual building blocks, we bridged them via oligo-p-phenyleneethynylenes of variable lengths by β-linkages and the Prato–Maggini reaction. With steady-state absorption, fluorescence, Raman, and XPS measurements we realized the basic physico-chemical characterization of the photo- and redox-active components and the multicomponent conjugates. Going beyond this, we performed transient absorption measurements and corroborated by single wavelength and target analyses that the selective (metal)porphyrin photocexcitation triggers a cascade of charge transfer events, that is, charge separation, charge shift, and recombination, to enable the directed charge flow. The net result is a few nanosecond-lived charge-separated state featuring a GNP-delocalized electron and a one-electron oxidized ferrocenium.

Introduction

In 2004, graphene moved into the center of attention when Geim and co-workers isolated for the first time single-layers of honeycomb networks based on sp²-hybridized carbon atoms by using adhesive tape. Ever since, two-dimensional graphene turned into the rising star in nanotechnology. All kinds of graphene materials were systematically explored in terms of their characterization and exploited in basic science as well as applications. Leading examples are found in the emerging areas of nanoelectronics, energy-storage, biosensors, and photoconversion systems. Graphene gives rise to outstanding electronic and mechanical features; high thermal conductivity and tensile strength just to mention a few. There is reason to believe that this material is ideally suited not only to outperform semiconducting silicon, but also to replace it, for example, in solid-state devices in the computer and micro- and nanoelectronics.

To demonstrate the wider applicability of graphene its poor solubility/dispersibility needs to be overcome. Attractors, which are based on π–π interactions between individual graphene layers, are the true bottleneck that needs to be tackled. Transformation by means of chemical functionalization based on the use of molecular building blocks is one of the very few high potential approaches toward the manipulation of the band gap in graphene. Among the molecular building blocks light harvesters such as porphyrins, phthalocyanines, etc. stand out. Their utilization allows for a much better overall stability of the respective graphene dispersions. In addition, it affords highly versatile functional materials with photo- and redox-active constituents.

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A sound understanding of graphene materials is essential for tuning those electronic communications and interactions that are needed for breakthroughs in technological applications. Of great importance is the band-gap design in graphene materials through chemical functionalization/doping to enable non-linear optics, photovoltaics, energy-storage, and biosensing. As of today, numerous examples of non-covalently functionalized graphene-based electron donor-acceptor systems exist, and they are well understood. Several chemical methodologies, which are based on well-established routes, have been developed to modify bulk graphite and, subsequently, to stabilize single and/or few layers of graphene. Cycloaditions, free-radical additions, and click reactions represent those organic reactions that are most frequently used when sp²-carbons of graphene are covalently functionalized. Among the aforementioned, cycloaditions of porphyrins to pristine graphene is the most promising choice. For example, Prato and co-workers reported that the 1,3-dipolar cycloadditions permit covalent functionalization of graphene through a condensation reaction. Aminoacids, on one hand, and carboxylic groups, on the other hand, react by forming iminium salts, which subsequently decarboxylate and yield azomethine ylides. As a consequence, fused pyrrolidines are incorporated onto the basal plane of graphene. In principle, multiple additions facilitate the introduction of several functional constituents in a single reaction step. Notably, this procedure has been extensively exploited for the chemical modification of fullerences, carbon nanotubes and carbon nanohorns with applications in various fields. In stark contrast, acylations are preferentially carried out with the graphene planes were intercalated with chemical substances such as sulphates and nitrates.

Considering the large-scale applications of few-layered graphene-based materials we have investigated for the first time the functionalization of a new carbon-based material: graphene nanoplates (GNP). GNP is best described as few layers of graphene, which is produced in high-yields in research-based laboratories. The design of graphene-based functional materials for charge-transfer applications requires suitable methods and choices of redox- and photo-active constituents.

What still remains as an open question is what causes the short lifetime of radical ion pair states upon either electron or hole injection into exfoliated graphene and/or few layers of graphene. In the case of few layers graphene, to which (metallo)phthalocyanines are linked in the form of either electron donors or acceptors, the lifetimes are limited to a few hundred picoseconds. The only approach that assists in addressing this question is to control the electron donor-acceptor distance. To the best of our knowledge, (metallo)porphyrins have never been used in combination with a secondary electron donor to functionalize few layers of graphenes. Setting up a versatile redox gradient along chains of multiple electron donor-acceptor enables cascades of short-range charge transfer events and, in turn, ensures the spatial separation of charges, that is, one-electron reduced and one-electron oxidized electron donors. In terms of molecular building blocks, we decided to explore (metallo)porphyrins and ferrocenes conjugates owing to their different strength of electron-donation. This approach is similar to that we explored in fullerene-based electron donor-acceptor conjugates, which exhibit long-lived charge-separated states as the product of a cascade of several charge-transfer events. In particular, we focused on the synthesis of β-modified porphyrins, which feature electron-accepting C₆₀ and/or electron-donating ferrocenes at the β-, meso-, or 4-phenyl positions. Our past work provided fundamental insights into the unambiguous identification of all the different species that evolve as products of any charge-transfer reactions, namely charge separation, charge shift, charge recombination, etc.

In light of our experience, we opted in this work for linking electron-donating ferrocenes (Fc) with light-harvesting electron-donating (metallo)porphyrins (ZnP) and electron-accepting graphene nanoplates (GNP) via oligo-p-phenyleneethynylene of variable lengths. A unique feature of our nanocarbon-based materials is the β-linkage at the (metallo)porphyrins to modulate the electron donor-acceptor interactions.

### Results and Discussion

#### Synthesis

The synthesis of GNP (Figure 1) was based on a low cost, fast, scalable, and stable fabrication method. It relies on a standard 800 W household microwave (MW) oven and starts with an Asbury® Expandable graphite sample, where the graphene planes were intercalated with chemical substances such as sulphates and nitrates.

After MW irradiation, the samples are best described by a worm-like morphology with a very large particle area. Using a short ultrasound treatment in isopropylic alcohol, the worm-like overall structures were removed from GNPs. Correspondingly, the 2D particles with lateral dimensions of tens of micrometers and thicknesses < 5 nm correspond to several layers of graphene.

The scanning electron microscope micrograph in Figure 1 confirmed that the intercalated multilayer graphite had undergone expansion. In fact, even if in the SEM microscope the electrons have typically a low energy of up to 30 keV. As such, nanometer thicknesses and the low atomic weights of carbon allowed electrons to pass, which rendered the underlying plates discernable.

![SEM image of graphene nanoplates (GNP).](image-url)
In Scheme 1, we summarize the synthetic strategy for obtaining the new GNP-conjugates. The first step involved the Sonogashira coupling of 1 (H\(_2\)Br\(_2\)) with 1.5 equivalents of 4-[(4'-ethynyl)phenyl]-ethynylbenzaldehyde 2, affording porphyrin derivative 3 in 36% yield after chromatographic purification.\(^1\) The stereochemistry of 2,12-dibromo-TPP (H\(_2\)Br\(_2\)) as starting material was recently elucidated.\(^2\) The next step was a second Sonogashira coupling reaction between 3 and two equivalents of three different electron donors, namely a–c, yielding the three different intermediates 4a,\(^3\) 4b,\(^4\) and 4c, in which the ferrocenes are linked to porphyrin by different spacers. By adopting a literature procedure, Zn\(^{II}\) ion was inserted in the cavity of the porphyrin to give 5a, 5b,\(^5\) and 5c in high yields. In the last step, the Prato-Maggini reaction\(^6\) was used to connect GNP to 5(a–c), and 5(a–c)-GNP were isolated. Each step of the reaction was characterized and confirmed using Mass spectrometry and NMR spectroscopy as reported in SI (from Figure S4 to Figure S9).

**Scheme 1.** Synthetic pathway towards the new GNP-conjugates.

**X-Ray Photoelectron Spectroscopy**

XPS analysis was performed with GNP before and after its functionalization to establish the differences between 5a, 5b, and 5c, on one hand, and 5a-GNP, 5b-GNP, and 5c-GNP, on the other. An example is given in Figure 2, in which the Fe 2p\(_{3/2}\) photoemission region a major peak evolves at 708.0 eV next to a low-intensity feature at 711.1 eV and a satellite line at higher energies. In agreement with literature reports,\(^7\) the Fe 2p main peak is assigned to Fe\(^{II}\), while the other two components originate from Fe\(^{III}\). The co-existence of Fe\(^{III}\) and Fe\(^{II}\) is likely to be due to interactions of the ferrocene valence orbitals with the conjugated network of \(\pi\)-orbitals in graphene. As a matter of fact, some of us have reported on a redox-active Si (100) hybrid system, to which fullerenes were covalently functionalized.\(^8\) In the present study, XPS spectra of Fe 2p revealed the presence of Fe\(^{III}\) and Fe\(^{II}\) in a different ratio with respect to the substituted ferrocenes directly bound to the same Si (100) via C=C or C=C anchors. The bonding between the Fe-ZnP and GNP fragments was corroborated by the presence of two distinct N 1s peaks, that
Porphyrin nitrogens (398.6 eV) and substituted amine groups (401.1 eV). From Figure 2b,a 4:1 ratio is described. The aforementioned results were expected based on linking 5b to GNP in 5b-GNP.

By virtue of an N/Fe atomic ratio, which is 5.0, and a Zn/Fe atomic ratio, which is 1.0, we confirm the intact nature of the attached Fe-ZnP fragments. Figure 2c displays the Zn 2p/2,1/2 photoemission region, which reveals a peak at 1022.4 eV, and, which confirms the presence of the (metallo)porphyrin.

Results for 5a-GNP (Figure S10) and 5c-GNP (Figure S11), which are summarized in the SI, attest the linkage of 5a and 5c, respectively, to GNP. 5-GNP (Figure S3), which was also characterized by XPS (Figure S12), was used as a reference in the transient absorption spectroscopy measurements.

**Raman Spectroscopy**

To validate the GNP functionalization with the different Fe-ZnP fragments, Raman spectra were compared. The Raman spectrum of 5a is dominated by the ZnP-centered fluorescence. Consequently, a correction of the Raman spectrum, by subtraction of the fluorescence, was performed. This is shown in Figure 3. Based on the ZnP fluorescence quenching in the conjugates, a well-resolved Raman spectrum evolves for 5a-GNP. The most intense peaks are attributed to graphene. For example, the G- and 2D-bands are discernable at 1580 and 2700 cm$^{-1}$ respectively. Additional peaks are seen at 852, 1001, 1234, 1492, and 1551 cm$^{-1}$ and they all relate to ZnP (Figure 3b). When turning to 5c-GNP (Figure S13), some subtle changes relative to 5a-GNP are evident. ZnP-centered peaks at 403, 592, and 1000 cm$^{-1}$ are noticeably enhanced.

![Figure 2](image)

*Figure 2. XPS spectra of 5b-GNP: a) Fe 2p$_{3/2}$, b) N 1s, and c) Zn 2p$_{3/2,1/2}$ photoemission regions with experimental data and peak-fits as dots and lines, respectively.*

![Figure 3](image)

*Figure 3. Raman spectra, using a 600 lmm$^{-1}$ grating, in the 200–3000 cm$^{-1}$ spectral range of a) 5a and b) 5a-GNP.*
To testify that the Fc-ZnP fragments are covalently linked in the conjugates to GNP rather than adsorbed, comparative assays were performed. A leading example is gathered in Figure 4, where a comparison between 5b-GNP and a mixture of GNP and 5b is shown. The Raman peaks at 1540 and 2200 cm\(^{-1}\), which are diagnostic probes for the presence of Fc-ZnP fragments, are present in both cases. But, any other peaks, related to the covalent bonding, are absent in the mixtures of GNP and 5b (Figure 4a). Peaks at 200, 300, 400, and 600 cm\(^{-1}\) (Figure 4b) are attributed to 5b vibrations. More important are, however, the peaks at 235 and 400 cm\(^{-1}\) as well as the intensity inversion of the peaks at 590 and 630 cm\(^{-1}\). All of them testify the covalent bonds between 5b and GNP. A spectral deconvolution implies that the peaks between 1250 and 1400 cm\(^{-1}\) are due to the superimposition of the GNP-centered D-band at around 1350 cm\(^{-1}\), and 5b vibrations around 1250 and 1400 cm\(^{-1}\). Please note that all of the peaks are well defined in the spectrum of the conjugate. When turning to the spectrum of the GNP and 5b mixtures, the GNP-centered D-band dominates, while those peaks, which are due to the Fe-ZnP fragments, are missing. Most important are the differences in the 1500–1600 cm\(^{-1}\) range.

An intensification of the 1500 cm\(^{-1}\) peak highlights the graphene-porphyrin linkage. The presence of the 1560 cm\(^{-1}\) shoulder suggests the formation of the five-membered ring obtained during the Prato-Maggini reaction.\(^{[50]}\)

To localize the binding sites between the GNP and Fe-ZnP fragments, Raman spectral imaging was carried out. The results for 5c-GNP are reported in Figure 5. In details, the G-band at 1579 cm\(^{-1}\) was used to map the GNP flakes (Figure 5a), while the peak at 1498 cm\(^{-1}\) to identify the presence of 5c (Figure 5b). On the GNP, the localization of unfunctionalized sites versus functionalized ones was concluded from the ratio of the peak area of the G-band at 1579 cm\(^{-1}\) relative to the peak area of 5c at 1498 cm\(^{-1}\).

The localization of the Fc-ZnP fragments, shown in Figure S13, was derived by analyses of the peak areas at 1498 cm\(^{-1}\). Higher values were correlated with the presence of the fragments at a specific site. As shown in Figure 5c, the images obtained for 5c-GNP through spectroscopic data highlight the homogeneous presence of Fc-ZnP fragments (Figure 5b) on the GNP surface (Figure 5a), confirmed by the ratio of peak areas.

On the contrary, the distribution of Fc-ZnP fragments on GNP in 5a-GNP is by far more heterogeneous (Figure S15). The corresponding spectra for 5b-GNP are displayed in Figure S14.

Atomic Force Microscopy

As a complement, atomic force microscopy (Figures S16–19) was performed with samples that were drop casted from THF dispersions onto clean silicon wafers. For all GNP-conjugates, next to residues stemming from solvents and Fe-ZnP fragments, graphene flakes with an average height of 5–
10 nm are present. This is, however, more than what we observed just for GNP. We attribute this finding to the porphyrins and the phenyl-ethynyls, which are likely to result into stronger stacking. All in all, the results indicate that the conjugates consists of multi-layered turbostratic graphene when studied in the solid state.

**Steady-State Absorption and Fluorescence Spectroscopy**

Various references were used in the following sections: commercially available zinc-tetraphenylporphyrin (ZnTPP), FeC-ZnP based conjugates (H2ZnPa, H2ZnPb, (Figure S1)), a β-substituted zinc porphyrin-based reference (β-ZnP-ref) (Figure S2), and 5-GNP (Figure S3).

Figures 6, S20, and S22 show the absorption spectra of the different GNP conjugates together with the ZnTPP and β-ZnP-ref references, respectively. Overall, β-substitution has a considerable influence on the absorption features, which include broadening and red-shifts relative to ZnTPP. Notably, the Soret-band absorption shifts from 427 nm in ZnTPP to 433 nm in 5-GNP, and 445 nm in β-ZnP-ref, 5a-GNP, 5b-GNP, and 5c-GNP. Likewise, the Soret-band absorptions split. Also, the ratio of the Q(0,0) to Q(1,0) band absorption is changed from 0.38 in ZnTPP to 0.69, 0.80, and 1.0 for 5-GNP, 5a-GNP, and 5b-5c-GNP respectively. This is indicative for the break in degeneracy of the 1E(000) levels.

From the absorption data, the band-gap of the GNP was determined by means of the Tauc analysis (see for details the S1). The direct band-gap is 3.1 eV, which reflects the semi-conducting nature of GNP (Figures S20, S21). By employing the Tauc analysis for the GNP absorption we observed a narrowing of the band-gap due to functionalization, with values in the range of 2.60–2.75 eV (Figure S23). [53-56]

To this end, the absorption spectra of 5a-Ca,[32] 5a-GNP, and ZnTPP (Figure S22b) give rise to subtle changes in the form of broadened and red-shifted absorption bands. All the changes in the electronic properties indicate that the molecular orbitals of ZnP are subjected to perturbation due to the steric effects and β-substitution.

Probing the excited-state interactions between the (metallo)porphyrins and GNP was realized by recording the fluorescence of ZnTPP as references and compared to that of 5-GNP, 5a-GNP, 5b-GNP, and 5c-GNP—Figures 7, S25, and S26a, b. At first glance, the fluorescence spectra of 5a-GNP, 5b-GNP, and 5c-GNP resemble that seen for ZnTPP. However, a notable red-shift of ≈ 20 nm confirms the more extended π-conjugation.[32,34,44] A closer look reveals a distance-dependent trend when comparing the ZnP fluorescence as a function of separation between the electron donating Fc and ZnP (Figure 7). For instance, 5-GNP, which lacks any Fc, exhibits a minimum of fluorescence quenching. This increase, however, in the following order: 5c-GNP < 5b-GNP < 5a-GNP. This trend clearly supports the notion that the addition of Fc as a second electron donor promotes an additional excited state deactivation. A likely rationale is a charge transfer, whose efficiency decreases with distance. In this context it is important to note that molecular orbital theory has underlined that the unique π-electron system of graphene acts as an electron acceptor when directly linked to a (metallo)porphyrin.[31] π-Stacking between electron-abundant aromatics and carbon materials is yet another cause for the fluorescence quenching.

**Electrochemical Studies**

To shed light on the electrochemical behavior of 5a-GNP, 5b-GNP, and 5c-GNP, cyclic voltammetry studies were carried out in acetonitrile. The GCEs were modified prior to the any of the measurements by drop casting the sample solutions (Scheme S1).

In Figure S27, the CVs of the Fc-ZnP fragments 5a, 5b, and 5c are displayed, as they assist in understanding the
interactions between Fc, ZnP, and GNP. From Figure S27a, which shows the cyclic voltammogram of 5a, we deduce a first, quasi-reversible oxidation at +0.69 V. This is Fe-centered. In addition, a second, irreversible oxidation is seen at +0.90 V, which is attributed to the ZnP oxidation. In terms of reduction, two irreversible steps are seen for 5a at −1.27 and −1.54 V. Both of them are ZnP-centered. 5b (Figure S27b) reveals a first, quasi-reversible oxidation at +0.59 V followed by a second, irreversible oxidation at +0.87 V. These are Fe- and ZnP-centered, respectively. The reduction is characterized by a first, reversible step at −1.28 V and a second, irreversible step at more negative values. For 5c, a reversible oxidation at +0.54 V is accompanied by two irreversible oxidations at +0.96 and +1.24 V and two irreversible reductions at −1.34 and −1.54 V, respectively (Figure S27c). Looking at the Fe-centered oxidation in 5a, 5b, and 5c we derive a notable distance dependence. In other words, the closer Fe is placed to ZnP, the stronger the shift to more positive oxidations is.

To study the interactions between Fe, ZnP, and GNP, CV measurements were also performed with 5a-GNP, 5b-GNP, and 5c-GNP. They are shown in Figure S28 and summarized in Table 1. Notable shifts are seen for 5a-GNP, 5b-GNP, and 5c-GNP relative to 5a, 5b, and 5c. With the help of the electrochemical and the steady-state absorption/fluorescence spectroscopy we employed the following equation,

\[ \Delta G_{\text{red}} = |e(E^a(D/D^*) - E^a(A/A^*))| - E_{\text{red}} (\text{ZnP}) \]  

(1)

to corroborate that the formation of Fe•••ZnP•••GNP is exergonic by ca. −0.2 eV relative to the energy of the ZnP first singlet excited state with 2.0 eV.[32,57] To evaluate the energetics of those charge-separated states which are based on the one electron reduced form of GNP, that is, Fe-ZnP•••GNP••• and Fe•••ZnP-GNP•••, we referred to the values reported in the literature for the reduction of graphene sheets. After correcting the reported values versus Ag/Ag⁺, the reduction was determined to be in the range from −0.5 to −0.8 V.[58,59] Interestingly, this value matches well with the reduction observed for 5c-GNP at −0.5 V. Therefore, formation of Fe•••ZnP-GNP••• (≈1.2 V) by means of a charge shift from Fe•••ZnP•••GNP••• (1.86 V) and Fc-ZnP•••GNP••• (≈1.55 V) is exergonic by at least −0.3 eV.

**Table 1:** Redox potentials of the Fe-ZnP fragments and GNP-conjugates recorded in argon-saturated acetonitrile with TBAPF₆ as supporting electrolyte, Ag/Ag⁺ as reference electrode, Pt as counter electrode, and glassy carbon as working electrode, at a scan rate of 0.01 V s⁻¹

| Compound | Oxidation | Reduction |
|----------|-----------|-----------|
|          | I         | II        | I         | II        |
| 5a       | +0.69     | +0.90     | −         | −1.27     | −1.54     |
| 5b       | +0.57     | +0.88     | −         | −1.28     | −1.53     |
| 5c       | +0.54     | +0.96     | +1.24     | −1.34     | −1.54     |
| 5a-GNP   | +0.51     | +0.94     | −         | −1.33     | −1.53     |
| 5b-GNP   | +0.56     | +0.90     | +1.15     | −1.31     | −         |
| 5c-GNP   | +0.56     | +0.88     | −         | −0.50     | −1.47     |

**Transient Absorption Spectroscopy**

To further elaborate on the excited state interactions, which were concluded from the steady-state fluorescence assays we performed transient absorption measurements and used an excitation wavelength of 460 nm. To interpret the dynamics in the reference as well as conjugates, the raw data were analyzed using multi-wavelength analyses and global target analyses.[60] The details are given in the experimental section.

Firstly, we looked at β-ZnP-ref. Upon excitation, singlet excited state features in the visible and the near-IR-regions evolve at around 500, 598, 620, and 1367 nm, next to the ground state bleaching at 578 and 618 nm. Based on multilength and the global analyses we gathered the best fit by employing a three species kinetic model (Figure S30a), which is in sound agreement with the deactivation model known for ZnTPP. Following Soret-band absorption excitation, the second singlet excited (1*ZnP) undergoes internal conversion to afford the first singlet excited state (1*ZnP) (SAS1) on an ultrafast fs-time scale, which we were unable to resolve. 1*ZnP is then subjected to intersystem crossing into 1.0 ns after the vibrational relaxation (1*ZnP) (SAS2) in 36.0 ps to generate the long-lived triplet excited state (1*ZnP) (SAS3) with characteristic transients at 498 and 920 nm (Figures S29 and S30).

Next, we turned to the GNP-conjugates. We looked first at 5-GNP as it provides important insights into understanding the essential interactions between (metallo)porphyrin and GNP and the dynamics thereof (Figure S31).[60] Relative to β-ZnP-ref, the 5-GNP conjugate exhibits upon 460 nm excitation not just the 1*ZnP-related features in the visible region, but also the GNP-centered phonon bleaching in the near-infrared region as SAS1. It is within 9.90 ps that SAS2 is formed, whose transient spectrum is positive and spans across the visible and the near-infrared regions. Of particular importance is the broad maximum, which ranges from 610 to 670 nm, and the positive transient in the near-infrared region. All of this resembles what has been summarized in the literature as the one-electron oxidized form of ZnP, on one hand, and the one-electron reduced form of GNP: ZnP•••GNP•••. The latter state charge recombinesthe energetically lower lying 3*ZnP as SAS3. 550 ps is the time that it takes for charge recombination (Figures S32 and S33).

The picture changes quite a bit, when probing 5a-GNP, 5b-GNP, and 5c-GNP. Concerning the conjugates, ZnP is excited and affords the second singlet excited state. It is the latter that is prone to undergo ultrafast internal conversion to yield the first singlet excited state. Upon excitation, the 1*ZnP singlet excited state with its characteristic maxima and minima in the visible region is directly formed, along with the GNP phonon bleaching in the NIR region was observed. Considering the redox gradient, which we corroborated in the electrochemical studies, we adopted a kinetic model from the previous work on electron accepting C₆₇Olinked to ZnP and Fc (Figures S34 and S35).[32] As a matter of fact, the model gave rise to a 100% convergence at a maximum of 40 iterations to fit the data qualitatively. Starting with the 5a-GNP (Figure S8a) in which Fc experiences the shortest separation...
between the Fcs and ZnPs due to the presence of either one or two phenyl-ethynyl subunits, the $^{3}$ZnP lifetime (SAS1) increases consecutively from 4.0 to 11.0 ps. Following the population from SAS1, the lifetimes of the Fc$^{+}$-ZnP$^{-}$-GNP (SAS2) charge recombination is fit with 38.5 ps for 5b-GNP, and 200 ps for 5c-GNP. On the other hand, Fc-ZnP$^{+}$-GNP$^{-}$ as SAS3 is subject in 5b-GNP to a charge recombination within 550 ps. It is, however, the ground state recovery and the triplet state population, which competes with the charge shift, to afford Fc$^{+}$-ZnP-GNP$^{-}$ as SAS4. SAS4 decays with a lifetime longer than the instrumental timescale. Additionally, SAS4 exhibits contributions from the coexisting $^{3}$ZnP.

In 5c-GNP (Figures 8b, and 9c,d), SAS3 shows, on one hand, ground state recovery with 1200 ps and, on the other, population of $^{3}$ZnP (SAS4) both as charge recombination processes. The Fc$^{+}$-ZnP-GNP$^{-}$ could not be observed for the 5c-GNP. This is probably due to the relatively low population of Fc$^{+}$-ZnP-GNP state stemming from the large distance between the Fc and ZnP. Subsequently Fc$^{+}$-ZnP-GNP$^{-}$, which is the product of charge-shift gets hardly populated. It is the concomitant formation of the $^{3}$ZnP, which dominates the differential absorption spectra across the entire spectral range on longer timescales.

**Conclusion**

We present the synthesis, characterization, and investigation of novel GNP-based electron donor-acceptor conjugates. For the first time, electron-donating ferrocenes (Fc) were combined with light-harvesting/electron-donating (metallico-)porphyrins (ZnP) and electron-accepting GNPs: Fc-ZnP-GNP. Different analytical and spectroscopic techniques have been applied to demonstrate the successful GNP functionalization: Mass spectrometry, NMR spectroscopy, XPS, and Raman spectroscopy coupled with Raman imaging. The covalent GNP functionalization enabled reproducible and comparative assays regarding the deactivation dynamics in the Fc-ZnP-GNPs, in which variable distances between the GNPs, ZnPs, and Fcs have been guaranteed by employing oligo-p-phenyleneethynlenes of variable lengths. Of great importance is the fact that cascades of charge-transfer events (Figure 10) generate long-lived charge-separated states featuring a GNP-delocalized electron and a one-electron oxidized ferrocenium. Key to this separation of charges is the simultaneous formation of two short-lived charge-separated states as intermediates, that is, Fc$^{+}$-ZnP$^{-}$-GNP and Fc-ZnP$^{-}$-GNP$^{-}$.

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Conflict of interest
The authors declare no conflict of interest.

Stichwörter: graphene nanoplates · zinc-tetraphenylporphyrin

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