DOI: 10.1002/chem.200902507

A Panchromatic Supramolecular Fullerene-Based Donor–Acceptor Assembly Derived from a Peripherally Substituted Bodipy–Zinc Phthalocyanine Dyad**

Yannick Rio,[a] Wolfgang Seitz,[b] Andreas Gouloumis,[a] Purificacion Vázquez,[a]
Jonathan L. Sessler,*[c] Dirk M. Guldi,*[b] and Tomás Torres*[a]

Abstract: A panchromatic 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene –zinc phthalocyanine conjugate (Bodipy–ZnPc) **1** was synthesized starting from phthalocyanine aldehyde **4**, via dipyrromethane **3** and dipyrromethene **2**. Conjugate **1** represents the first example in which a Bodipy unit is tethered to the peripheral position of a phthalocyanine core. Electrochemical and optical measurements provided evidence for strong electronic interactions between the Bodipy and ZnPc constituents in the ground state of **1**. When conjugate **1** is subjected to photoexcitation in the spectral region corresponding to the Bodipy absorption, the strong fluorescence characteristic of the latter subunit is effectively quenched (i.e., $\geq 97\%$). Excitation spectral analysis confirmed that the photoexcited Bodipy and the tethered ZnPc subunits interact and that intraconjugate singlet energy transfer occurs with an efficiency of ca. 25%. Treatment of conjugate **1** with *N*-pyridylfulleropyrrolidine (**8**), an electron-acceptor system containing a nitrogen ligand, gives rise to the novel electron donor–acceptor hybrid **1**↔**8** through ligation to the ZnPc center. Irradiation of the resulting supramolecular ensemble within the visible range leads to a charge-separated Bodipy–ZnPc$^{\bullet+}$–C$_{60}$$^{\bullet-}$ radical-ion-pair state, through a sequence of excited-state and charge transfers, characterized by a remarkably long lifetime of 39.9 ns in toluene.

Keywords: Bodipy · charge transfer · energy transfer · fullerenes · phthalocyanines · supramolecular chemistry

Introduction

In recent years, inspired in large measure by a desire to mimic the natural photosynthetic processes, major efforts have been devoted to developing systems with energy and/or electron-transfer functions.[1,2] Within the context of this overarching goal, 18 π-electron aromatic phthalocyanines (Pc)[3] have emerged as particularly promising building blocks for the construction of covalent and noncovalent donor–acceptor conjugates and supramolecular assemblies. In fact, in combination with other electroactive moieties, especially electron acceptors, such as fullerenes[4,5] and perylenes,[6] their use has led to systems with attractive photoinduced charge-separation characteristics. The motivation to use Pc is largely driven by their particular optical and electrochemical features, combined with their documented photochemical stability.[3] The intense absorptions of Pc, not only in the near-UV (Soret bands at 350 nm), but also in the near-IR (Q bands at 700 nm) where the maximum of the solar photon flux occurs, are essentially unique among easily accessible synthetic chromophores.[7] This makes Pc-based

---

[a] Dr. Y. Rio, Dr. A. Gouloumis, Prof. P. Vázquez, Prof. T. Torres
Departamento de Quimica Organica
Universidad Autonoma de Madrid
Cantoblanco, 28049 Madrid (Spain)
Fax: (+34) 91-497-3966
E-mail: tomas.torres@uam.es

[b] W. Seitz, Prof. D. M. Guldi
Department of Chemistry and Pharmacy
& Interdisciplinary Center for Molecular Materials
University of Erlangen-Nürnberg
Egerlandstrasse 3, 91058 Erlangen (Germany)
Fax: (+49) 913-1852-8307
E-mail: dirk.guldi@chemie.uni-erlangen.de

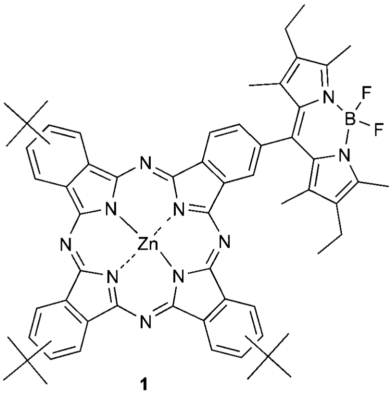
[c] Prof. Dr. J. L. Sessler
Department of Chemistry & Biochemistry
The University of Texas at Austin
Austin, TX 78712-0165 (USA)
Fax: (+1) 512471-7550
E-mail: sessler@mail.utexas.edu

[**] Bodipy = 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200902507.

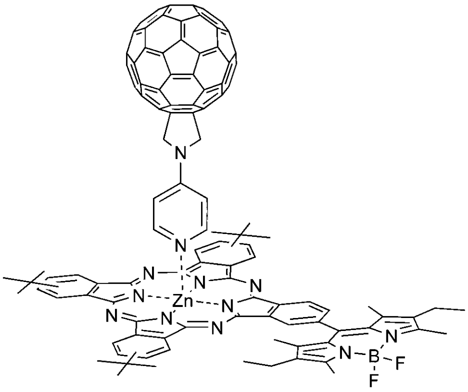
systems among the most promising molecular constructs currently being studied in the area of artificial solar technology.[8]

In spite of their advantages, a major limitation for the use of Pc in creating functional devices is that they do not absorb well over the full visible spectrum (i.e., between the dominant Soret- and Q-band transitions). This is especially true in the context of developing solar cells, in which broad photosensitization effects would be desirable. To date, a variety of structural modifications have been made in an effort to address this limitation, such as the insertion of different metals and peripheral functionalization. However, the resulting benefits have been limited to the induction of red- or blueshifted Soret and Q bands; modifications that still leave a rather broad spectral range without significant absorptions.[7] An attractive alternative strategy for expanding the absorption features of Pc-based systems as a whole would involve attaching a chromophoric unit to the Pc framework that 1) absorbs in a spectral region complementary to that of Pc, and 2) is capable of transferring its excited-state energy in a unidirectional fashion to the Pc core. Such a strategy has already been used to good effect in the creation of Pc constructs with porphyrins[9] or subphthalocyanines.[10] However, it has yet to be generalized in terms of using other chromophores. Among the possible additional chromophores, the spectral features of which would complement those of Pc, are derivatives of 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene, a species more commonly known as Bodipy.[11,12] Bodipy derivatives generally display strong absorption in the visible spectral region and possess high fluorescence quantum yields for emission maxima that range from 490 to 650 nm. In fact, several studies have already described excited-state interactions between Bodipy derivatives, which act as light-harvesting subunits, and energy acceptors such as porphyrins,[13] perylenediimides,[14] subphthalocyanines,[15] and axially substituted phthalocyanines.[16] However, to the best of our knowledge, no examples of covalently linked, peripherally substituted Bodipy–phthalocyanine conjugates have been reported to date. We describe herein the first such system, the Bodipy–Pc conjugate **1**. This system functions as a panchromatic light-harvesting system that absorbs light over a broad spectral range and is able to undergo efficient internal-energy transduction.



1

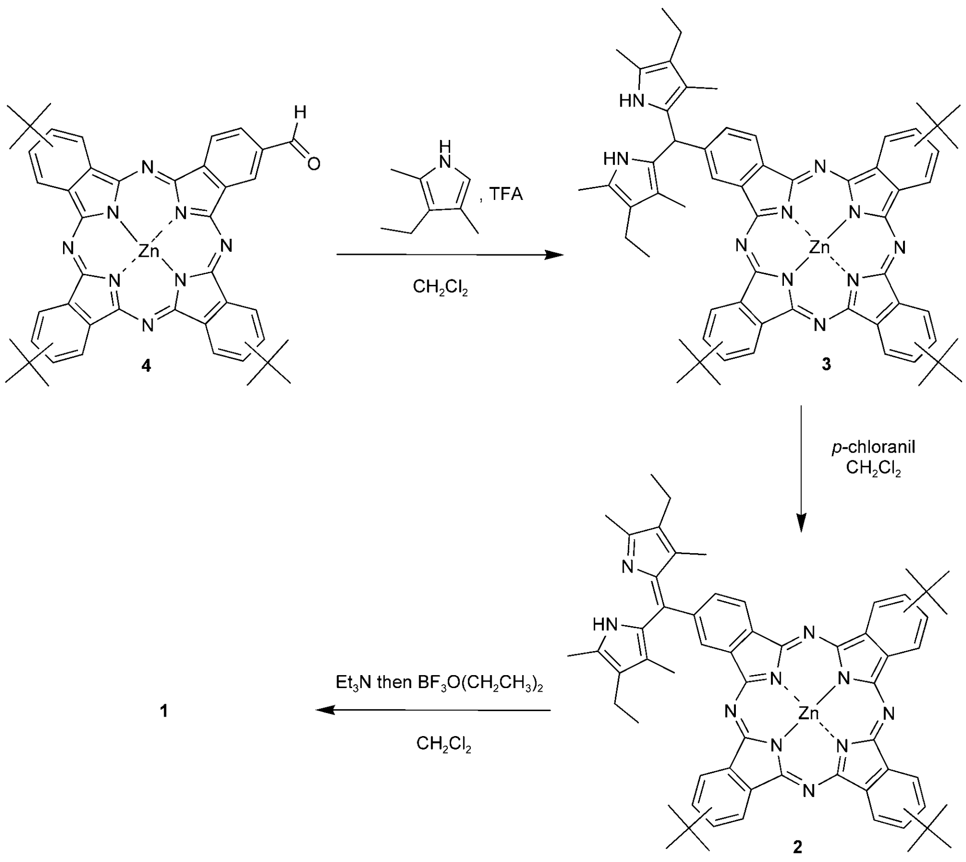
Recently, the first example of an axially coordinated Bodipy–silicon phthalocyanine (SiPc) hybrid was published.[16] Our approach differs from this earlier system in that a direct, peripheral linkage is used to tether the Bodipy chromophore to the ZnPc core. This leaves the metal free for axial ligation and permits the further construction of supramolecular motifs through metal complexation. If this coordination is used to tether a further electroactive species, such a supramolecular approach could provide a versatile and facile entry into complex electron donor–acceptor architectures. A variety of ligands with electroactive constituents have already been developed and shown to self-assemble successfully with the metal centers of porphyrins and phthalocyanines to produce ensembles capable of undergoing photoinduced electron-transfer reactions.[5c,17] In particular, C_{60} derivatives functionalized with either pyridine[18] or imidazole[19] were found to form photo- and redox-active electron donor–acceptor hybrids with ZnPc. In light of this precedent, we have chosen *N*-(4-pyridiyl)-3,4-fulleropyrrolidine **8**[18a] as a ligand and, as detailed below, have found that it will self-assemble with **1** to form a new and unprecedented electron donor–acceptor hybrid, Bodipy–ZnPc–C_{60} (**1**↔**8**). Photoirradiation of the resulting three-component complex **1**↔**8** produces a long-lived, charge-separated (radical ion pair) state, Bodipy–$ZnPc^{\bullet+}$–$C_{60}^{\bullet-}$, that ultimately decays to produce the ground state. This system differs from earlier systems in that it contains both a Bodipy–phthalocyanine and a zinc phthalocyanine–fullerene connection, as opposed to either couple on its own.



1↔**8**

Results and Discussion

Synthesis: Among the methods known to prepare Bodipy derivatives,[11] one of the more efficient is a three-step procedure[20] that involves first forming a dipyrromethane derivative through the acid-catalyzed condensation of an aldehyde and pyrrole. This condensation step is followed by an oxidation to yield the corresponding dipyrromethene derivative and subsequent treatment with boron trifluoride etherate. Applying this strategy to the construction of target conjugate **1** required a formylphthalocyanine, which could then be reacted with an appropriately chosen pyrrole. Given the expected need to enhance solubility, we chose the tri-*tert*-butyl-formylphthalocyanine **4**, an intermediate described previously by our research group.[21] 3-Ethyl-2,4-dimethylpyrrole was chosen as the pyrrole to avoid the formation of undesired side products.[22] Condensation of these two precursors in dichloromethane under acidic conditions afforded dipyrromethane **3**, as shown in Scheme 1. Dipyrromethane **3** was not isolated; rather, it was oxidized in situ by treatment with *p*-chloranil to give the corresponding dipyrromethene **2**. Following flash chromatographic purification on alumina, compound **2** was subject to deprotonation (treatment with triethylamine) and treated with boron trifluoride etherate to afford the Bodipy–ZnPc conjugate **1** in an overall yield of 28%.

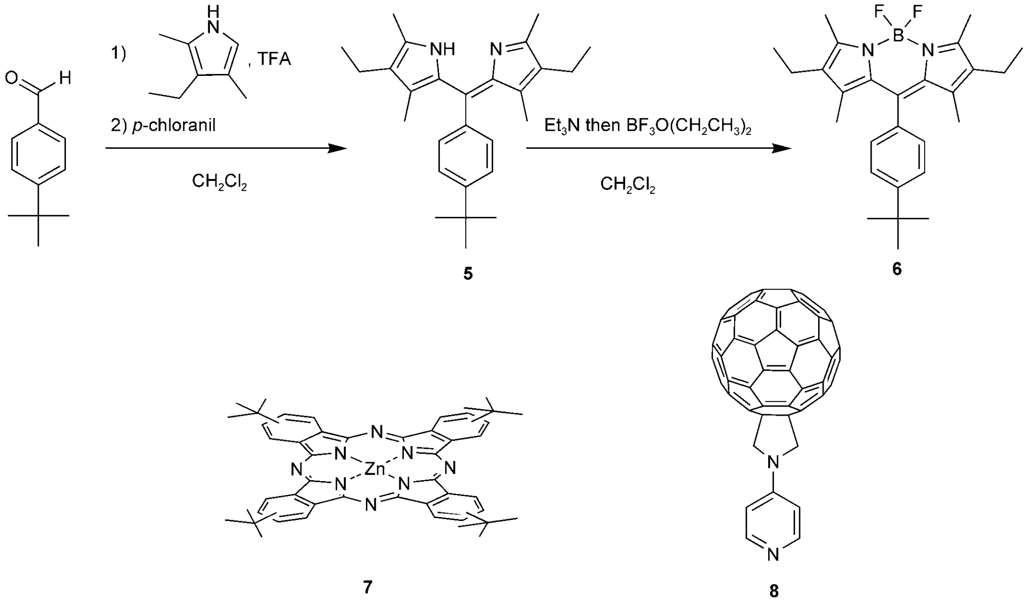


Scheme 1. One-pot, three-step synthesis of **1**.

A slightly revised procedure was employed to prepare a Bodipy reference compound (**6**; Scheme 2). In this case, 3-ethyl-2,4-dimethylpyrrole was condensed with *tert*-butylbenzaldehyde in dichloromethane under acidic conditions. This was followed by oxidation with *p*-chloranil, deprotonation with triethylamine, and reaction with boron trifluoride etherate to effect boron complexation.

Compounds **1** and **6** were characterized by means of mass spectrometry, elemental analysis, and absorption and NMR spectroscopies (see the Supporting Information). The tendency of Pc to form aggregates, especially at the concentrations required to acquire reasonable NMR spectra complicated analyses in the case of **1** (Figure S6 in the Supporting Information). The isolation of positional isomers of **1** reflects the fact that starting material **4**[21] is a regioisomeric mixture, and rendered the recording and interpretation of the ^1H NMR spectrum difficult. Nevertheless, MALDI mass spectrometry provided evidence for the formation of the intermediate dipyrrin **2** and the final Bodipy–ZnPc conjugate **1**, as did combustion analyses in the case of the latter species. Absorption spectroscopic studies provided additional confirmation of the formation of **2** and **1**. In particular, the UV/Vis spectrum of dipyrrin–ZnPc **2** (Figure 1) proved to be quite similar to that of an ordinary Pc displaying, for example, the symmetrical features seen for tetra-*tert*-butyl ZnPc **7** (a 350 nm Soret band and 679 nm Q-band transition). The effect of boron chelation and conversion to hybrid **1** is also apparent on inspection of Figure 1. For instance, a 2 nm redshift in the Pc-based Q band is observed. In addition, an intense absorption band centered at 529 nm, characteristic of a Bodipy complex including specifically reference compound **6**, is seen in **1** that is not present in the boron-free precursor **2**. Such spectral features, when combined with those of the ZnPc, give rise to a panchromatic system that absorbs over a large portion of the visible spectral region. Additional support for the proposed boron complexation came from ^1H NMR spectroscopic analyses. For instance, all of the aliphatic methylene protons in **6**, and those that could be identified in the spectrum of **1**, exhibited the chemical shifts expected for a boron–dipyrrin complex.

Electrochemistry: The solution electrochemistry of **1**, and of the Bodipy and ZnPc reference compounds **6** and **7**, was studied by using cyclic voltammetry (CV). The data are presented in Figure 2 and are collected in Table 1.



Scheme 2. Synthesis of the Bodipy reference system **6** and depictions of the ZnPc reference compound **7** and the N-pyridylfulleropyrrolidine electron acceptor **8**.

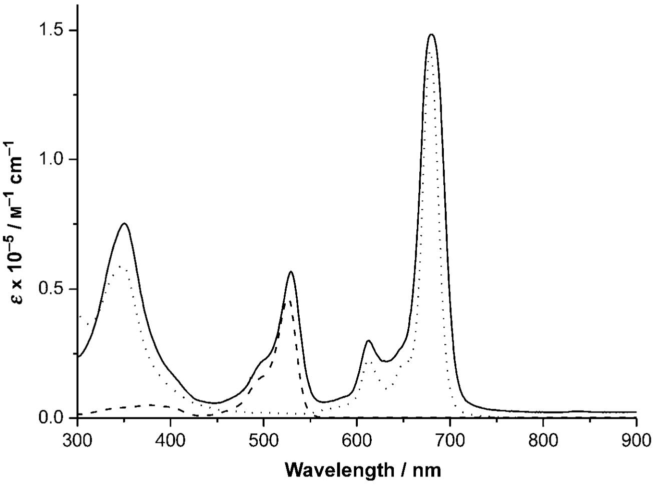


Figure 1. Absorption spectra of Bodipy reference **6** (dashed line), ZnPc reference **7** (dotted line), and Bodipy–ZnPc **1** (solid line) recorded in toluene.

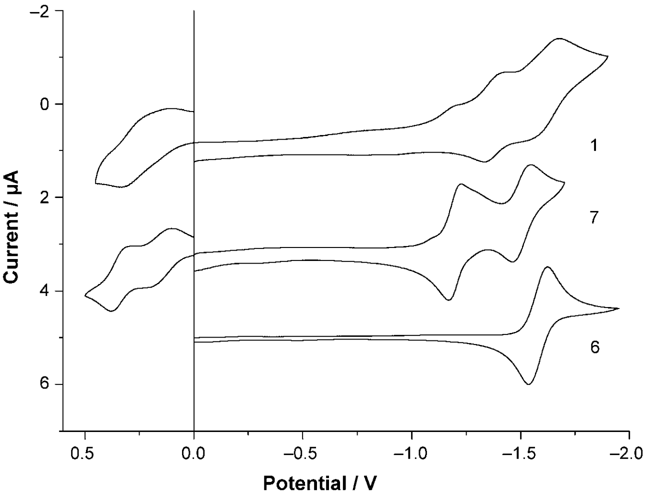


Figure 2. Cyclic voltammograms of compounds **1**, **7**, and **6** as determined in acetonitrile in the presence of 0.1 M $TBAClO_4$ (used as the supporting electrolyte). See the Supporting Information for further details of these analyses.

Bodipy–ZnPc conjugate **1** is electrochemically active in both the anodic and cathodic sweep directions; that is, redox processes are seen upon scanning between 0.6 and −2.0 V (see Figure 2). In the cathodic scan, system **1** exhibits two reversible reduction peaks at around −1.38 and −1.59 V, respectively. The first one-electron reduction process correlates well with the first reduction of ZnPc. The second process involves two electrons and is ascribed to the overlapping reductions of Bodipy (first reduction wave) and ZnPc (second reduction wave) based on comparisons with the reference systems **6** and **7**. To the extent these assignments are correct, the two ZnPc-based reductions in **1** are

Table 1. Electrochemical data (V vs. $Ag/AgNO_3$) corresponding to the redox processes of compounds **1**, **6**, and **7** as determined by CV analyses (sweep rate = 0.1 $V s^{-1}$) carried out in acetonitrile (0.1 M $TBAClO_4$) at room temperature. All measurements were carried out under identical experimental conditions. Errors are estimated at ±25 mV for the tabulated values.

	E_{red}^2 [V]	E_{red}^1 [V][a]	E_{ox}^1 [V]	E_{ox}^2 [V]
1	−1.59[a,b,c]	−1.38[a]	0.13[d]	0.29[d]
6	–	−1.58	–	–
7	−1.50	−1.20	0.14	0.34

[a] Pc-based reduction. [b] Bodipy-based reduction. [c] Two-electron unresolved process. [d] Two-electron poorly resolved process.

shifted to more negative values by 180 and 90 mV, respectively, relative to **7**.

In the anodic scan, conjugate **1** reveals an electrochemically irreversible, two-electron oxidation process ($\Delta E_p = 240$ mV), which is poorly resolved even at scan rates of 20 to 600 mV s^{-1}. Based on a comparison with **7**, this oxidation process is believed to reflect the coalescence of the two ZnPc oxidation processes, tentatively assigned as occurring at 0.13 and 0.29 V, respectively. On this basis, it is thought that the second ZnPc oxidation is shifted in the negative direction by 50 mV. Such a shift, mirroring what is seen upon reduction, is taken as evidence of electronic communication between the Bodipy and ZnPc subunits in the ground-state form of **1**.

Considering the well-documented tendency of ZnPc to interact with various axial ligands, including C_{60} derivatives functionalized with either pyridine or imidazole metal ligating groups, we postulated that **1** could be used to create the photoactive ensemble **1**↔**8** by treatment with *N*-(4-pyridiyl)-3,4-fulleropyrrolidine (**8**). As a first step towards characterizing this putative supramolecular ensemble, we analyzed the electrochemical features of both the ZnPc reference (**7**) and the target Bodipy–ZnPc conjugate **1** in the presence of the C_{60} derivative **8** (affording **7**↔**8**, and **1**↔**8**, respectively). In addition to the aforementioned Bodipy- and ZnPc-centered process, we note the expected first, second, and third one-electron reductions of C_{60} at −0.95, −1.33, and −1.85 V versus Fc/Fc$^+$, respectively. Considering the first one-electron ZnPc oxidation (**7**↔**8**: +0.08 V; **1**↔**8**: 0.32 V) and the first one-electron C_{60} reduction (**7**↔**8**: −0.95 V; **1**↔**8**: −0.95 V), different radical-ion-pair-state energies evolve (**7**↔**8**: 1.03 V; **1**↔**8**: 1.28 V).

Photophysical properties: Further insights into the electronic interactions between the Bodipy and ZnPc constituents in **1** came from absorption spectroscopic studies (Figure 1). Bodipy is characterized, among other things, by strong absorption features in the blue spectral region ($\lambda_{max} = 525$ nm), which are assigned to S_0–S_1 transitions. Likewise, ZnPc gives rise to S_0–S_1 transitions that are substantially redshifted relative to those of Bodipy ($\lambda_{max} = 680$ nm; Q band). In addition, S_0–S_2 transitions are discernable at 350 nm (B band). In the Bodipy–ZnPc conjugate **1**, all of the Bodipy- and ZnPc-centered features are readily discernible, with maxima that are shifted bathochromically by around 3 nm. Although not large, such shifts are consistent with the ground-state interactions inferred from the electrochemical studies. A preliminary molecular modeling study has been carried out; it shows that the Bodipy and ZnPc planes are not completely orthogonal. Such a relative orientation allows for a degree of orbital overlap and is expected to favor the observed electron delocalization between the two subunits.

An initial characterization of the excited-state properties of **1** was made by using steady-state fluorescence spectroscopy. Here, it was found that subjecting ZnPc **7** to irradiation in the region of the S_0–S_1 transitions (at $\lambda_{ex} = 660$ nm), gives rise to a strong fluorescence emission in the red spectral region ($\lambda_{em} = 690$ nm), for which a quantum yield of 0.30 has been established (Figure 3). Similarly, when exciting **1** at 660 nm, the wavelength at which the ZnPc moiety absorbs preferentially, a ZnPc-centered fluorescence was seen. A comparison of the λ_{em} with that of **7** reveals a bathochromic shift of about 2 nm, which parallels the modest differences seen in the absorption features of **7** and **1**. The overall quantum yield of 0.27 is similar to that seen for **7**.

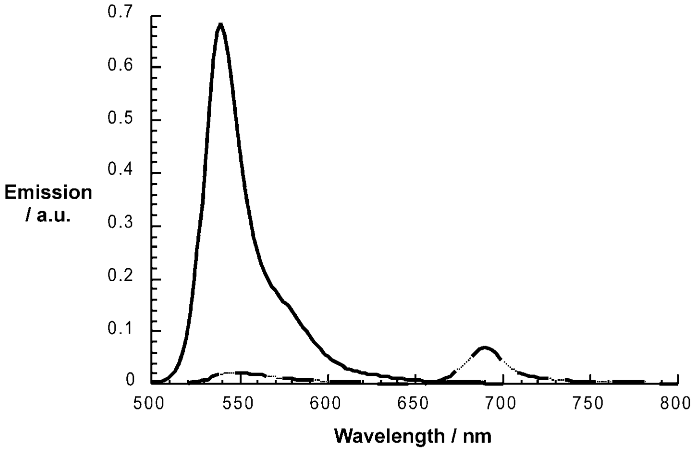


Figure 3. Steady-state fluorescence spectra, recorded in toluene with excitation at 480 nm, of Bodipy reference **6** (solid line) and Bodipy–ZnPc **1** (dashed line) with matching absorption at the excitation wavelength at room temperature.

Much greater differences were seen when the photophysical properties of **1** were compared with those of the Bodipy reference system **6**. This latter reference compound displays a quantum yield of 0.68, and as expected for complexes of this type, gives rise to an emission at around 540 nm when excited at or near its absorption λ_{max}. In marked contrast, when **1** is excited in the region of Bodipy absorption, essentially no fluorescence emission from this latter chromophore is seen (the quantum yield is ca. 0.02 for the Bodipy fluorescence). Rather, emission is seen in the red portion of the spectrum, with ZnPc-like fluorescence features being seen at 680 nm. As the ZnPc absorption is minimal at the excitation wavelength, we interpret such findings in terms of singlet-state energy transfer from the photoexcited Bodipy to the ZnPc core. Based on the ZnPc fluorescence quantum yield (0.07 in the case of **1**), the efficiency of this energy transduction process is calculated to be approximately 25 %.

The fluorescence properties of **1** and the associated control system **6** were examined in greater detail by carrying out time-resolved measurements using time-correlated, single-photon-counting techniques (Figure 4). When the Bodipy reference system **6** was subject to photoexcitation at 467 nm in solvents such as toluene and THF, an analysis of the 540 nm fluorescence signal revealed a lifetime of 5.4 ns. In stark contrast, exciting **1** at 467 nm produced no detectable fluorescence signal at 540 nm within the lower time limit of our experimental setup (200 ps). However, when this

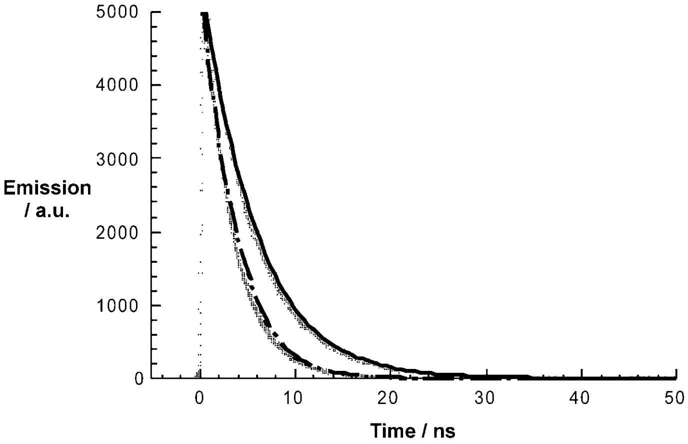


Figure 4. Time-resolved fluorescence spectra (TCSPC) of Bodipy reference **6** recorded at 540 nm (solid line; photoexcitation at 467 nm), Bodipy–ZnPc **1** at 690 nm (dotted line; photoexcitation at 467 nm), and ZnPc reference **7** at 690 nm (dashed line; photoexcitation at 647 nm).

same 467 nm excitation process was monitored at 690 nm (i.e., at the ZnPc fluorescence wavelength), a lifetime of 3.1 ns was obtained for **1**. A similar lifetime was also derived when either **6** or **1** was subject to photoexcitation at 647 nm (i.e., at the ZnPc absorption wavelength). Such observations are consistent with the ultrafast energy-transfer scenario inferred from the steady-state measurements described above.

Further confirmation for the proposed energy-transfer hypothesis was obtained from an analysis of the excitation spectra. By following the ZnPc fluorescence at 700 nm, excitation spectra of **1** could be recorded; these were found to exhibit the spectral characteristics of ZnPc at 350, 610, and 680 nm, as would be expected were energy transfer taking place. However, as shown in Figure S12 in the Supporting Information, an additional spectral signature, namely, that of Bodipy at 525 nm, is also seen; this is consistent with a contribution from the Bodipy subunit to the overall fluorescence profile of the mixed Bodipy–ZnPc conjugate **1**.

Femtosecond transient absorption spectroscopy was used to obtain further insights into the excited-state interactions in the Bodipy–ZnPc conjugate **1** and to corroborate the proposed energy-transfer process. The reference systems ZnPc **7** (Figure S13 in the Supporting Information) and Bodipy **6** (Figure S14 in the Supporting Information) together with hybrid **1** (Figures 5 and 6), were probed with 150 fs laser pulses. Either 520 or 680 nm excitation was used to excite the Bodipy and ZnPc constituents, respectively. In the case of ZnPc **7**, the singlet excited state, which is formed essentially right after the laser pulse, includes a broad transient maximum at 490 nm, a transient bleaching between 610 and 680 nm, and another transient maximum at 810 nm. These features correlate with what would be expected for an S_0–S_1 transition involving the ground state of ZnPc. The singlet transient produced upon photoexcitation of **7** decays with a lifetime of 3.0 ns by intersystem crossing into the corresponding triplet manifold. The main spectral features of the latter state consist of a maximum at 500 nm and two minima

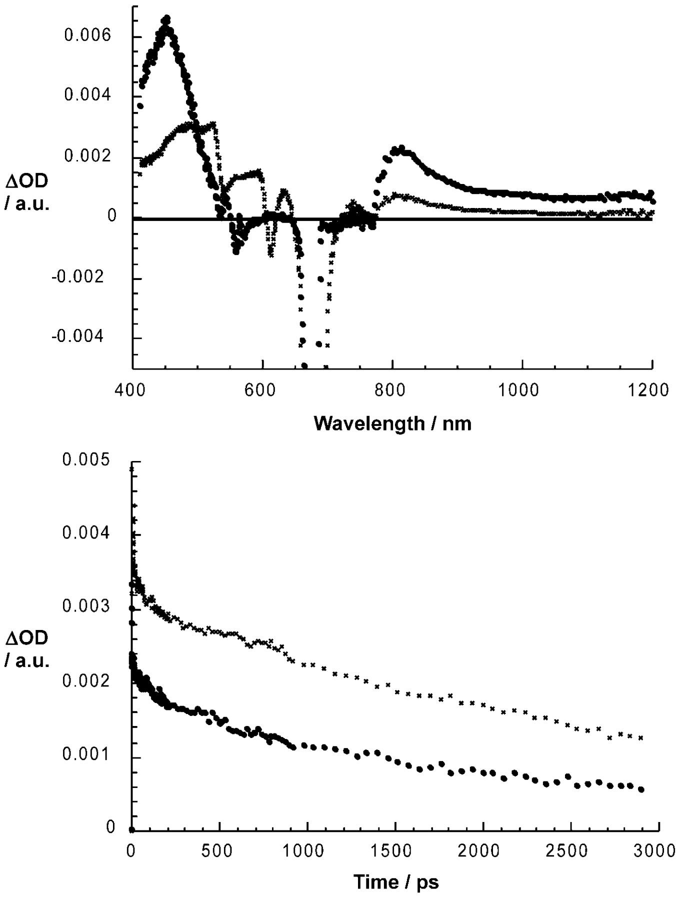


Figure 5. Top: Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (680 nm) of **1** ($\approx 10^{-6}$ M) in argon-saturated toluene with time delays of 5 (filled circles) and 3000 ps (crosses). Bottom: Time versus absorption profiles at 595 (crosses) and 812 nm (filled circles) of the spectra shown above, monitoring the intersystem crossing in toluene.

at 350 and 680 nm. In the absence of molecular oxygen, the triplet state relaxes slowly to the ground state within about 120 µs.

In the case of the Bodipy reference system **6**, excitation at 387 or 520 nm gives rise to transient absorption changes immediately after the laser pulse that are dominated by a ground-state bleaching in the 540 nm spectral range. These features decay within 5.6 ns in toluene—a value that is in excellent agreement with the lifetime derived from the fluorescence lifetime measurements (5.4 ns) discussed above. Again, this value is consistent with conversion to the triplet ground state.

Subjecting **1** to 680 nm excitation gives rise to the same spectral features as were recorded for ZnPc **7**. However, in the case of **1**, additional ground-state bleaching was observed in the spectral region corresponding to the Bodipy absorption, that is, around 530 nm. The intersystem crossing, for which a lifetime of 3.1 ns is estimated, is not affected by the presence of the Bodipy subunit.

A very different picture emerges when a 520 nm laser pulse is used to photoexcite **1**. In this case, formation of the

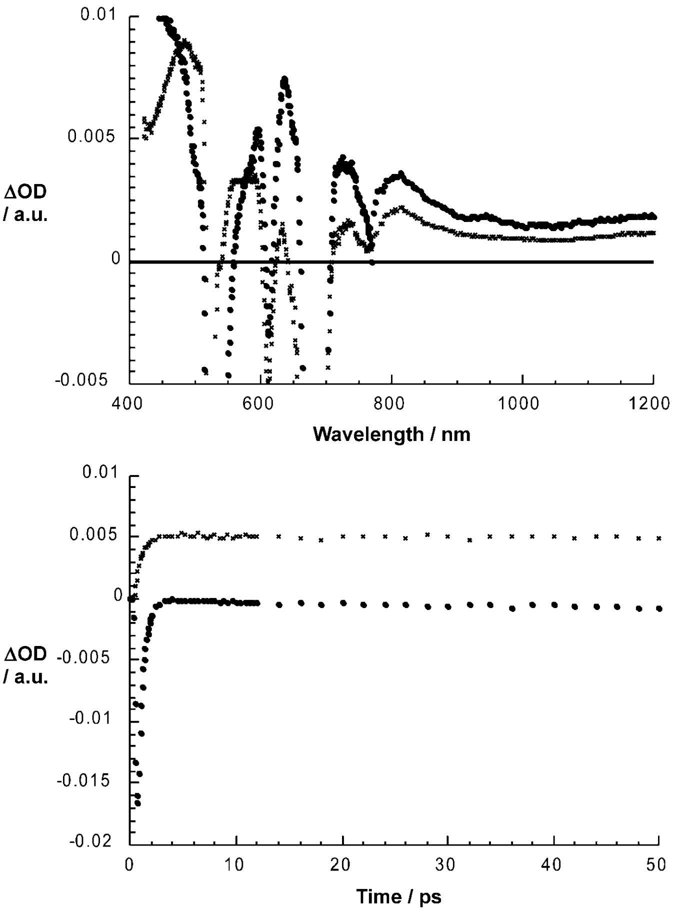


Figure 6. Top: Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (520 nm) of **1** ($\approx 10^{-6}$ M) in argon-saturated toluene with time delays of 5 (filled circles) and 3000 ps (crosses). Bottom: Time versus absorption profiles at 545 (filled circles) and 812 nm (crosses) of the spectra shown above, monitoring the energy transfer in toluene.

singlet excited state of Bodipy is observed right after the laser pulse, as inferred from the observation of a transient bleaching feature at 545 nm. In contrast to what is seen with the Bodipy reference system **6** (see above), the decay of this presumed singlet excited state of **1** is remarkably fast ($5 \times 10^{11}\ s^{-1}$) and is complete within 2 ps. The product of this decay process is not the triplet excited state of Bodipy, but rather the ZnPc singlet excited state, as determined from the observation of the characteristic spectral features at 490 and 810 nm. Importantly, the ZnPc singlet-excited-state formation kinetics of ≈ 2 ps are a qualitative match for those corresponding to the Bodipy singlet-excited-state decay. This value is consistent with a strong electronic coupling between the Bodipy and ZnPc subunits in the excited state. However, the poor spectral overlap between the Bodipy fluorescence and the ZnPc absorption renders the actual energy transduction process rather inefficient (25 %); see above.

In the final part of our investigations, we sought to take advantage of the complexation chemistry of the ZnPc moiety and produce a three-component supramolecular ensemble, Bodipy–ZnPc–C_{60} (**1**↔**8**).[23] Motivation for generating this particular ensemble came from an appreciation that the oxidation potentials of the ZnPc subunit in **1** were anodically shifted relative to those of the ZnPc reference **7**. This shifting raises the energy of the radical-ion-pair state in **1** and could provide a potent means of retarding the undesired charge recombination in the case that a "follow-up" electron-transfer reaction could be engendered. We considered it probable that use of the functionalized electron acceptor *N*-(4-pyridiyl)-3,4-fulleropyrrolidine (**8**), through coordination to the ZnPc moiety, would allow for such a follow-up electron-transfer process.

With the goal of producing **1**↔**8** and testing its viability as a charge-separating device, conjugate **1** was subject to titration with **8**. As in previous examples,[24] axial coordination of C_{60} was expected to take place at ZnPc, thus affording the electron donor–acceptor hybrid, Bodipy–ZnPc–C_{60} (**1**↔**8**). Indeed, as detailed below, all available evidence leads us to conclude that this hybrid is not only formed, but that is also produces a long-lived charge-transfer state upon appropriate photoexcitation.

As illustrated in Figure 7, quite drastic quenching of the ZnPc fluorescence is seen when C_{60} (in the form of **8**) is titrated into a solution of **1** in toluene. Over the concentration range tested (2.0×10^{-7}–2.0×10^{-5} M) the fluorescence intensity drops to less than 7 % of the initial value. In other words, the quenching in **1**↔**8**, in which C_{60} is presumed to be axially coordinated to ZnPc, exceeds 93 % regardless of direct ZnPc excitation (100 %) or indirect Bodipy-derived photosensitization (25 %). Such changes are fully consistent with an efficient charge-transfer process taking place between the photoexcited ZnPc and C_{60}. Corresponding titration experiments with **1** and a C_{60} derivative that lacks the coordinating pyridine functionality leads to the observation of absorption features that are a simple linear sum of the individual features and, in the case of the corresponding fluorescence spectra (Figure 7 and Figure S15 in the Supporting Information), to an insignificant quenching of the original ZnPc-centered features.

The observed exponential concentration/fluorescence relationship was used to quantify the association between **1** and **8**. To do this, the intensity data at 690 nm were recorded and plotted versus the C_{60} concentration (Figure 7). The binding profile obtained in this way was typical of a 1:1 association process. Nonlinear curve fitting allowed the association constant for the interaction of **8** with **1** to be calculated; the resulting K_a was $(1.7 \pm 0.2) \times 10^6\ M^{-1}$. This large association constant is, on one hand, consistent with what has been observed for the formation of a 1:1 complex between **8** and ZnPor (Por = tetraphenylporphyrin) for which a K_a of $10^5\ M^{-1}$ has been recorded.[18b] On the other hand, it reflects the weakening of the in-plane $Zn{-}N_{pyrrole}$ coupling (ZnPc versus ZnP) and the strengthening of the axial $Zn{-}N_{pyridine}$ bond.[4f]

The fluorescence quantum yields at the plateau values were also used to evaluate the dynamics of the excited-state

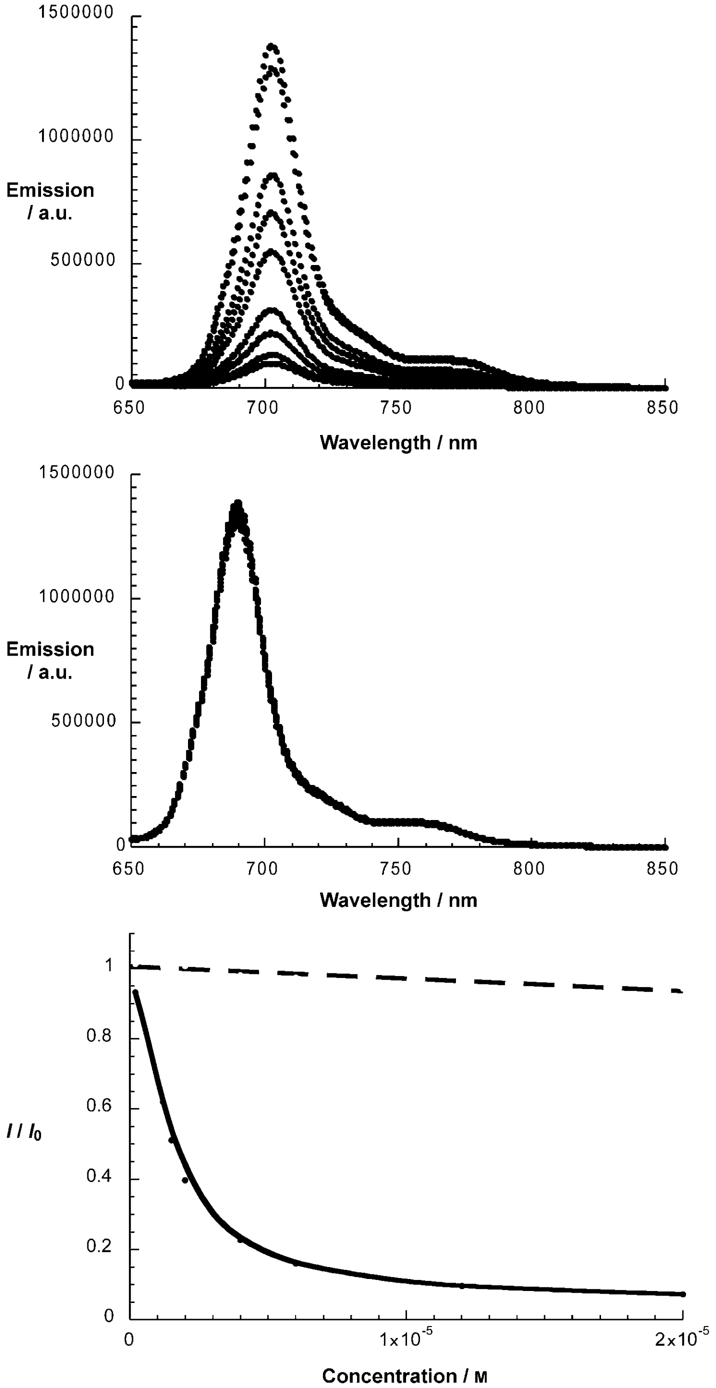


Figure 7. Top: Steady-state fluorescence spectra ($\lambda_{ex}=540$ nm) of **1** (2.0×10^{-6} M) recorded at different concentrations of **8** ($0–2.0\times10^{-5}$ M) in nitrogen-saturated toluene at room temperature. Middle: Steady-state fluorescence spectra ($\lambda_{ex}=540$ nm) of **1** (2.0×10^{-6} M) recorded at different concentrations of a C$_{60}$ reference ($0–2.0\times10^{-5}$ M) in nitrogen-saturated toluene at room temperature. Bottom: Plot of I/I_0 versus [**8**] (solid line) and I/I_0 versus [C$_{60}$ reference] (dashed line) used to determine the association constant.

deactivation process in **1**↔**8**. By comparing the relative quantum yields of the ZnPc subunits in **1** (for which an intersystem crossing rate constant of 1.8×10^{8} s^{-1} was calculated from the intrinsic decay of the singlet excited state; see above) and **1**↔**8** (in which strong quenching was observed), a charge-transfer rate constant of 3×10^{9} s^{-1} could be calculated.

Transient absorption spectroscopy confirmed the proposed charge-transfer mechanism. Immediately after subjecting the ensemble **1**↔**8** to a 150 fs laser pulse at 520 nm, the formation of the Bodipy singlet excited state is seen, as evidenced by its signature bleaching at 545 nm. As in the case of **1**, in the absence of added **8**, energy transfer occurs with a rate constant of 5×10^{11} s^{-1} to produce the ZnPc singlet excited state, inferred from the observation of the characteristic spectral features at 490 and 810 nm. However, in contrast to what is seen in **1**, a further charge-separation process takes place in the supramolecular ensemble **1**↔**8**, as detailed below.

Figure 8 illustrates that the ZnPc singlet excited state produced following laser excitation of **1**↔**8** at 520 nm is metastable and transforms rapidly (4.7×10^{10} s^{-1}) into a new species. As this occurs, spectral features characteristic of the one-electron oxidized form of ZnPc and the one-electron reduced form of C$_{60}$ are seen to grow at 840 and 1010 nm, respectively. Such a spectral evolution is consistent with a process of intraensemble charge transfer that yields a Bodipy–ZnPc$^{\bullet+}$–C$_{60}^{\bullet-}$ radical-ion-pair state. Within the instrumental detection range of our femtosecond setup, that is, 3 ns, this Bodipy–ZnPc$^{\bullet+}$–C$_{60}^{\bullet-}$ photoproduct is stable. In analogous experiments with **1** and a C$_{60}$ derivative that lacks the coordinating pyridine functionality only the formation of the ZnPc singlet excited state features (680 nm excitation) and Bodipy singlet excited state/ZnPc singlet excited state features (520 nm excitation) are seen.

In complementary nanosecond experiments, exciting at 532 nm, the near-infrared region displays the same differential absorption changes that were seen during the femtosecond experiments (Figure 9). A multiwavelength analysis of the time versus absorption profiles in the 840 (ZnPc$^{\bullet+}$) and in the 1020 nm (C$_{60}^{\bullet-}$) spectral ranges leads to a radical-ion-pair-state lifetime of 39.9 ns (2.5×10^{7} s^{-1}). Beyond this time window, only residual absorption features ascribed to the ZnPc triplet excited state can be observed, namely, a broad transient at 500 nm, followed by a weaker transient in the 800 nm region (see Figure 9). This is consistent with an evolution of the charge-separated state to produce a long-lived triplet state (at an energy level of ≈1.2 eV relative to the ground state). However, the quantum yield for the production of this triplet state is quite low (i.e., less than 5 % as inferred by the comparative method using **7**), leading us to conclude that mostly (i.e., 95 %) direct recombination to the ground state occurs.

When the control ZnPc system **7**, an electron donor–acceptor hybrid lacking the Bodipy functionality, was studied in the presence of the coordinating electron acceptor **8**, a similar charge-transfer evolution was seen following photoexcitation of the ZnPc subunit. However, in stark contrast to what was seen in the case of ensemble **1**↔**8**, the lifetime for the complex produced in the case of this control system

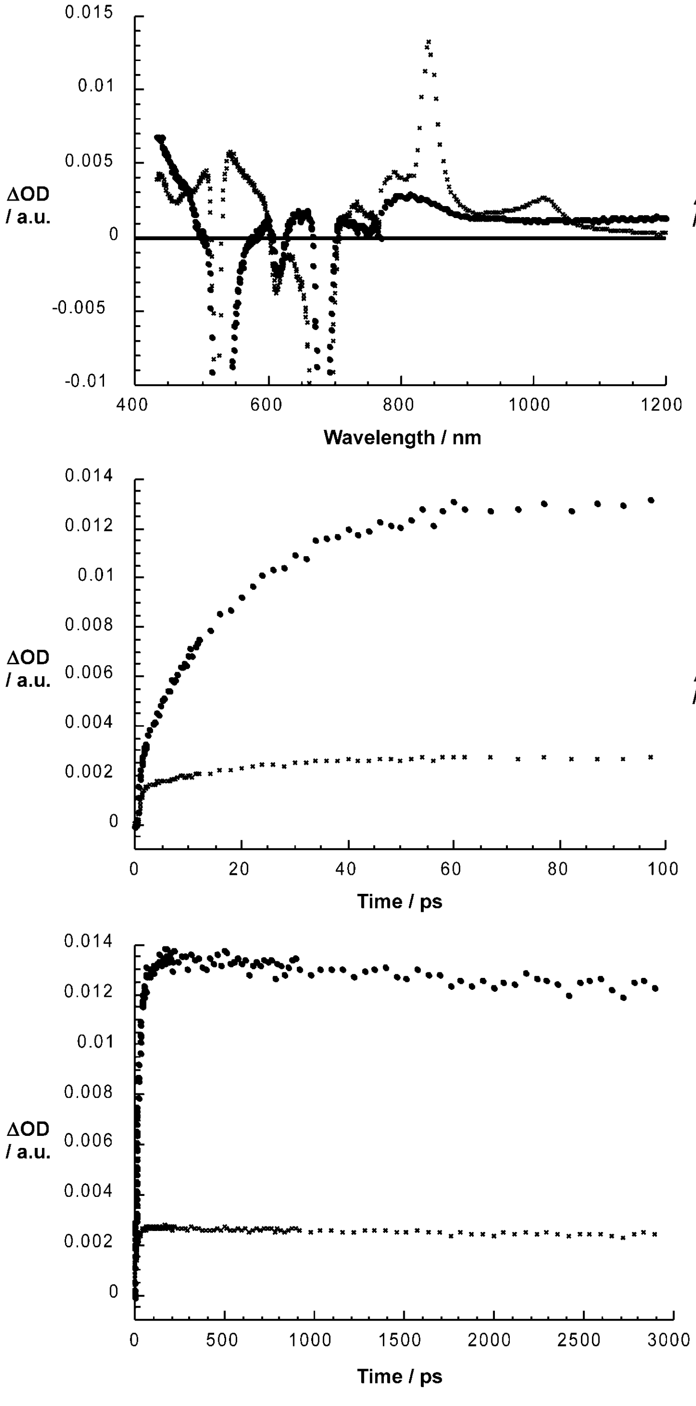


Figure 8. Top: Differential absorption spectra (visible and near-infrared part) obtained upon femtosecond flash photolysis (520 nm) of **1**↔**8** ($\approx 10^{-6}$ M) in argon-saturated toluene with time delays of 5 (filled circles) and 100 ps (crosses). Middle: Time versus absorption profiles at 842 (filled circles) and 1010 nm (crosses) of the spectra shown above, monitoring the energy-transfer and charge-separation processes in toluene. Bottom: Time versus absorption profiles at 842 (filled circles) and 1010 nm (crosses) of the spectra shown above, illustrating the stability of the charge separation.

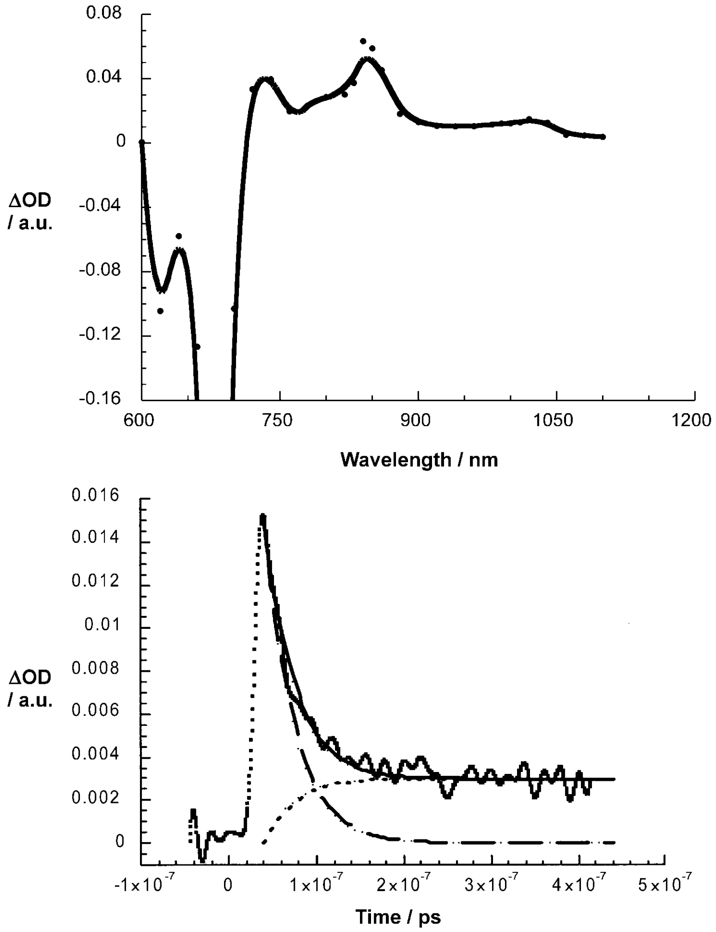


Figure 9. Top: Differential absorption spectra (visible and near-infrared part) obtained upon nanosecond flash photolysis (532 nm) of **1**↔**8** ($\approx 10^{-6}$ M) in argon-saturated toluene with a time delay of 10 ns at room temperature. Bottom: Time versus absorption profile at 1000 nm (black line) of the spectra shown above, monitoring the charge recombination process in toluene and the corresponding kinetic simulation of the time versus absorption profile using ACUCHEM with the rate constants stated above (ZnPc triplet-excited-state formation: dotted line; $C_{60}^{\cdot-}$ decay: dashed line; sum of both: solid line).

(ensemble **7**↔**8**) is less than 5 ns (i.e., the rate constant for charge recombination is $>2.0\times10^{8}\,s^{-1}$). On this basis, we propose that the Bodipy subunit not only plays a useful role in light harvesting, but also serves to stabilize the radical-ion-pair state produced following photoexcitation of the supramolecular ensemble **1**↔**8**. Another set of control experiments led us to test **1** with a C_{60} derivative (0–10^{-5} M) that lacks the coordinating pyridine functionality. Here, the only appreciable transient that could be observed was that associated with the ZnPc triplet excited state of **1**. The spectral evolution of this feature was consistent with this state being subject to a near-diffusion-controlled deactivation ($7.7\times10^{7}\,M^{-1}s^{-1}$). However, this putative deactivation process did not give rise to any stable photoproduct, as far as we could detect. In line with previous studies, we rationalize this latter finding to a lack of sufficient solvent stabilization, toluene in the present instance, to allow for the generation of an observable intermolecular radical-ion-pair state.[4]

Conclusion

In summary, a novel, panchromatic Bodipy–ZnPc conjugate **1** has been designed, synthesized, and probed with respect to its intramolecular energy- and charge-transfer reactions. Importantly, conjugate **1**, absorbing in two disparate but complementary sections of the solar spectrum (Bodipy: 525 nm; ZnPc: 680 nm), represents the first example in which a Bodipy unit has been linked covalently to a peripheral position of ZnPc. In this hybrid there is considerable electronic interaction between the photo- and redox-active constituents, namely, ZnPc and Bodipy, in the ground state. Upon being subject to photoexcitation at 480 nm, an intramolecular transduction of singlet-excited-state energy occurs; this funnels the excitation from the light-absorbing and energy-donating Bodipy (2.3 eV) to the energy-accepting ZnPc (1.8 eV) subunit. The net result is photosensitization of the ZnPc moiety by means of Bodipy photoexcitation.

In the absence of an added electron acceptor, neither kinetic nor spectroscopic evidence has been found that would support the notion of charge transfer (as opposed to energy transduction) between the Bodipy and ZnPc constituents. When such an acceptor is present, specifically a C_{60} moiety provided through pyridine coordination of **8** to the ZnPc metal center (resulting in formation of the electron donor–acceptor hybrid **1**↔**8** as noted above), a sequence of energy- and electron-transfer reactions occur following photoexcitation. Taken together, these serve to convert the Bodipy singlet excited state formed immediately upon photoexcitation into a Bodipy–$\mathrm{ZnPc}^{\bullet+}$–$\mathrm{C}_{60}^{\bullet-}$ radical-ion-pair state (1.28 eV) with an overall conversion efficiency of 25%. The lifetime of this charge-separated state reaches a remarkable value of 39.9 ns in toluene. This stands in marked contrast to what is seen in a reference system consisting of the ensemble produced through the interaction of ZnPc **7** and the pyridine-functionalized C_{60} system **8** (i.e., **7**↔**8**), in which the lifetime is less than 5 ns. The differences in radical-ion-pair-state lifetimes are attributed in part to the anodic shifts of the ZnPc oxidation potential produced as the result of linking a Bodipy subunit to the zinc phthalocyanine in the case of **1** (but not **7**). This change in energetics persists upon complexation of **8**, such that the free-energy changes associated with the charge recombination are greater in **1**↔**8** than in **7**↔**8** (specifically, 1.28 vs. 1.03 eV). This shifts the driving force for charge recombination deeper into the Marcus inverted region and serves to retard, as desired, the rate of $\mathrm{ZnPc}^{\bullet+}$ radical cation–$\mathrm{C}_{60}^{\bullet-}$ radical anion recombination in the more elaborate three-component supramolecular ensemble **1**↔**8**, relative to the simpler two-component system **7**↔**8**. The present work serves to illustrate not just the benefits that can accrue from linking a Bodipy subunit to a Pc core, but also the advantages of using the principles of self-association to produce strongly coupled Pc-based electron-active molecules for energy- and/or electron-transfer purposes.

Experimental Section

General: Details about solvent purification, instrumentation, and photophysical methods are provided in the Supporting Information.

Dyad 1: One drop of trifluoroacetic acid (TFA) was added to a degassed solution of tri-*tert*-butylformylphthalocyaninatozinc(II) (50 mg, 0.06 mmol) and 2,4-dimethyl-3-ethylpyrrole (16 mg, 0.13 mmol) in dry dichloromethane (10 mL). The solution was stirred at room temperature for allowing 4 h for the complete consumption of aldehyde **4**. *p*-Chloranil (16 mg, 0.06 mmol) was added and the resulting mixture stirred overnight. The reaction mixture was washed with water, then the organic layer was separated, dried over $MgSO_4$, and the solvent evaporated under reduced pressure. The crude compound was purified by flash column chromatography (Al_2O_3, 4:1 $CHCl_3/CH_3OH$) to afford a purple powder (38 mg) containing dipyrrin **2** as supported by mass spectrometry. MS (MALDI-TOF, dithranol): m/z: 999.4 $[M+H]^+$ (see Figure S4 in the Supporting Information); UV/Vis ($CHCl_3$): $\lambda_{max}=351$, 679 nm. In this particular case, the ^1H NMR spectrum is quite uninformative, showing broad signals that are ascribed to the strong aggregation of the compound at the concentration required for analysis. ^1H NMR (300 MHz, $[D_6]DMSO$, 25 °C, TMS): $\delta=0.97$–1.35 (m, 12H), 1.63–1.91 (m, 27H), 2.17–2.52 (m, 10H), 7.24–9.16 ppm (m, 14H). Boron trifluoride diethyl etherate (0.4 mL, 0.32 mmol) was added to a solution of **2** (33 mg, 0.03 mmol) in a mixture of dichloromethane (2 mL) and triethylamine (1 mL). The mixture was stirred at room temperature for 3 h. The solution was washed with water, and then the organic layer was separated and dried over Na_2SO_4. The crude compound was purified by flash column chromatography (SiO_2, 4:1 $CHCl_3/CH_3OH$) to afford a purple solid (16 mg, 28% overall yield). M.p. >220 °C; ^1H NMR (300 MHz, $[D_6]DMSO$, 25 °C, TMS): $\delta=0.70$–1.20 (m, 6H), 1.30–1.37 (m, 6H), 1.60–1.80 (m, 27H), 2.15–2.30 (m, 4H), 2.35–2.45 (m, 6H), 8.05–8.35 (m, 4H), 9.15–9.75 ppm (m, 8H); IR (KBr): $\tilde{\nu}=752$, 833, 914, 1080, 1259, 1327, 1491, 1612, 2955, 3393 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} $(\log\varepsilon)=350$ (4.9), 529 (4.7), 680 nm (5.2); MS (MALDI-TOF, dithranol): m/z: 1047.4 $[M+H]^+$; elemental analysis calcd (%) for $C_{61}H_{61}BF_2N_{10}Zn\cdot1.5\,H_2O$: C 68.13, H 6.00, N 13.02; found: C 68.18, H 6.27, N 12.85.

Compound 6: One drop of TFA was added to a degassed solution of 4-*tert*-butylbenzaldehyde (135 mg, 0.83 mmol) and 2,4-dimethyl-3-ethylpyrrole (208 mg, 1.71 mmol) in dry dichloromethane (10 mL). The solution was stirred at room temperature for 4 h for complete consumption of the aldehyde. *p*-Chloranil (206 mg, 0.84 mmol) was added and the solution was stirred overnight at room temperature. After evaporation of the solvent under reduced pressure, the crude product was purified by flash column chromatography (Al_2O_3, CH_2Cl_2/CH_3OH 5:1) to afford a brown solid. The resulting dipyrrin was then dissolved in a mixture of dichloromethane (10 mL) and triethylamine (5 mL) and treated with boron trifluoride diethyl etherate (0.3 mL, 4.15 mmol). The solution was stirred at room temperature for 3 h, washed with water, and the organic phase was separated and dried over Na_2SO_4. The crude product was then purified by flash column chromatography (SiO_2, 4:5 hexanes/$CHCl_3$) to afford an orange solid (76 mg, 21%). M.p. >220 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta=0.97$ (t, $J=7$ Hz, 6H), 1.19 (s, 6H), 1.36 (s, 9H), 2.27 (q, $J=7$ Hz, 4H), 2.32 (s, 6H), 7.21 (d, $J=8$ Hz, 2H), 7.42 ppm (d, $J=8$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta=11.4$, 12.5, 14.6, 17.1, 31.4, 34.8, 125.8, 153.4, 127.8, 131.0, 132.7, 138.5, 152.2 ppm; UV/Vis ($CHCl_3$): λ_{max} $(\log\varepsilon)=526$ nm (4.7); MS (MALDI-TOF, dithranol): m/z: 436.3 $[M]^+$; elemental analysis calcd (%) for $C_{27}H_{35}BF_2N_2\cdot0.5\,H_2O$: C 72.81, H 8.15, N 6.29; found C 72.70, H 7.88, N 6.23.

Acknowledgements

Grants from the Ministerio de Ciencia y Tecnología (CTQ2008-00418/BQU, Consolider-Ingenio 2010 CSD2007-00010 Nanociencia Molecular, ESF-MEC MAT2006-28180-E, SOHYDS), Comunidad de Madrid MADRISOLAR, S-0505/PPQ/0225) and the European Union (COST ActionD35, SOLAR n-TYPE, MRTN CT-2006-035533) are gratefully acknowledged. We also would like to thank the Deutsche Forschungsgemeinschaft (SFB 583), FCI and Office of Basic Energy Sciences of the U.S. Department of Energy for financial support. The work in Austin was supported by the Robert A. Welch Foundation (F-1018) and the National Science Foundation (CHE 0749571). J.L.S. and A.G. would also like to thank the Spanish Ministry of Education for a Sabbatical fellowship (SAB 2002-0153) and a Ramon y Cajal contract, respectively.

---

[1] a) *Artificial Photosynthesis: From Basic Biology to Industrial Application* (Eds.: A. F. Collings, C. Critchley), Wiley-VCH, Weinheim, **2005**, p. 313 ; b) M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435–461; c) D. Gust, T. A. Moore, A. L. Moore, *Theor. Chem. Acc.* **2001**, *34*, 40–48; d) H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults, William Tumas, *Chem. Rev.* **2001**, *101*, 953–996; e) S. Chakraborty, T. J. Wadas, H. Hester, R. Schmehl, R. Eisenberg, *Inorg. Chem.* **2005**, *44*, 6865–6878; f) V. Balzani, M. Clemente-León, A. Credi, B. Ferrer, M. Venturi, A. H. Flood, J. F. Stoddart, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 1178–1183.

[2] a) G. F. Moore, M. Hambourger, M. Gervaldo, O. G. Poluektov; T. Rajh, D. Gust, T. A. Moore, A. L. Moore, *J. Am. Chem. Soc.* **2008**, *130*, 10466–10467; T. Rajh, D. Gust, T. A. Moore, A. L. Moore, *J. Am. Chem. Soc.* **2008**, *130*, 10466–10467; b) A. C. Rizzi, M. van Gastel, P. A. Liddell, R. E. Palacios, G. F. Moore, G. Kodis, A. L. Moore, T. A. Moore, D. Gust, S. E. Braslavsky, *J. Phys. Chem. A* **2008**, *112*, 4215–4223; c) S. Fukuzumi, T. Kojima, *J. Mater. Chem.* **2008**, *18*, 1427–1439; d) R. F. Kelley, S. J. Lee, T. M. Wilson, Y. Nakamura, D. M. Tiede, A. Osuka, J. T. Hupp, M. R. Wasielewski, *J. Am. Chem. Soc.* **2008**, *130*, 4277–4284; e) A. C. Benniston, *Phys. Chem. Chem. Phys.* **2007**, *9*, 5739–5747; f) Y. Nakamura, N. Aratani, A. Osuka, *Chem. Soc. Rev.* **2007**, *36*, 831–845; g) A. Satake, Y. Kobuke, *Org. Biomol. Chem.* **2007**, *5*, 1679–1691; h) S. Gadde, D.-M. S. Islam, C. A. Wijesinghe, N. K. Subbaiyan, M. E. Zandler, Y. Araki, O. Ito, F. D'Souza, *J. Phys. Chem. C* **2007**, *111*, 12500–12503; i) H. Imahori, S. Fukuzumi, *Adv. Funct. Mater.* **2004**, *14*, 525–536; j) H. Imahori, Y. Mori, Y. Matano, *J. Photochem. Photobiol. C* **2003**, *4*, 51–83; k) D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **2001**, *34*, 40–48; l) N. Armaroli, G. Marconi, L. Echegoyen, J.-P. Bourgeois, F. Diederich, *Chem. Eur. J.* **2000**, *6*, 1629–1645.

[3] a) G. de La Torre, C. G. Claessens, T. Torres, *Chem. Commun.* **2007**, 2000–2015; b) C. G. Claessens, U. Hahn, T. Torres, *Chem. Rec.* **2008**, *8*, 75–97; c) *The Porphyrin Handbook, Vols. 15–20* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2003**.

[4] a) M. Quintiliani, A. Kahnt, T. Woeffle, W. Hieringer, P. Vázquez, A. Goerling, D. M. Guldi, T. Torres, *Chem. Eur. J.* **2008**, *14*, 3765–3775; b) B. Ballesteros, G. de La Torre, T. Torres, G. L. Hug, G. M. A. Rahman, D. M. Guldi, *Tetrahedron* **2006**, *62*, 2097–2101; c) A. de La Escosura, M. V. Martinez-Diaz, D. M. Guldi, T. Torres, *J. Am. Chem. Soc.* **2006**, *128*, 4112–4118; d) M. A. Loi, P. Denk, H. Hoppe, H. Neugebauer, C. Winder, D. Meissner, C. Brabec, N. S. Sariciftci, A. Gouloumis, P. Vázquez, T. Torres, *J. Mater. Chem.* **2003**, *13*, 700–704.

[5] a) T. G. Linssen, K. Durr, M. Hanack, A. Hirsch, *J. Chem. Soc. Chem. Commun.* **1995**, 103–104; b) K. Dürr, S. Fiedler, T. Linssen, A. Hirsch, M. Hanack, *Chem. Ber.* **1997**, *130*, 1375–1378; c) M. E. El-Khouly, O. Ito, P. M. Smith, F. D'Souza, *J. Photochem. Photobiol. C* **2004**, *5*, 79–104; d) Z. Tian, C. He, C. Liu, W. Yang, J. Yao, Y. Nie, Q. Gong, Y. Liu, *Mater. Chem. Phys.* **2005**, *94*, 444–448; e) K. N. Kim, C. S. Choi, K.-Y. Kay, *Tetrahedron Lett.* **2005**, *46*, 6791–6795; f) Y. Chen, M. E. El-Khouly, M. Sasaki, Y. Araki, O. Ito, *Org. Lett.* **2005**, *7*, 1613–1616; g) M. Isosomppi, N. V. Tkachenko, A. Efimov, H. Vahasalo, J. Jukola, P. Vainiotalo, H. Lemmetyinen, *Chem. Phys. Lett.* **2006**, *430*, 36–40; h) M. E. El-Khouly, E. S. Kang, K.-Y. Kay, C. S. Choi, Y. Aaraki, O. Ito, *Chem. Eur. J.* **2007**, *13*, 2854–2860; i) M. A. Loi, P. Denk, H. Hoppe, H. Neugebauer, D. Meissner, C. Winder, C. J. Brabec, H. Lehtivuori, T. Kumpulainen, A. Efimov, H. Lemmetyinen, A. Kira, H. Imahori, N. V. Tkachenko, *J. Phys. Chem. C* **2008**, *112*, 9896–9902; j) M. Niemi, N. V. Tkachenko, A. Efimov, H. Lehtivuori, K. Ohkubo, S. Fukuzumi, H. Lemmetyinen, *J. Phys. Chem. A* **2008**, *112*, 6884–6892; k) S. Fukuzumi, T. Honda, K. Ohkubo, T. Kojima, *Dalton Trans.* **2009**, *30*, 3880–3889; l) D. González-Rodríguez, G. Bottari, *J. Porphyrins Phthalocyanines* **2009**, *13*, 624–636; m) F. D'Souza, O. Ito, *Chem. Commun.* **2009**, 4913–4928.

[6] a) S. Fukuzumi, K. Ohkubo, J. Ortiz, A. M. Gutierrez, F. Fernandez-Lazaro, A. Sastre-Santos, *Chem. Commun.* **2005**, *30*, 3814–3816; b) M. S. Rodríguez-Morgade, T. Torres, C. Atienza Castellanos, D. M. Guldi, *J. Am. Chem. Soc.* **2006**, *128*, 15145–15154; c) Y. Chen, Y. Lin, M. E. El-Khouly, X. Zhuang, Y. Araki, O. Ito, W. Zhang, *J. Phys Chem. C* **2007**, *111*, 16096–16099; d) H. Lehtivuori, T. Kumpulainen, M. Hietala, A. Efimov, H. Lemmetyinen, A. Kira, H. Imahori, N. V. Tkachenko, *J. Phys. Chem. C* **2009**, *113*, 1984–1992.

[7] Y. Rio, M. S. Rodríguez-Morgade, T. Torres, *Org. Biomol. Chem.* **2008**, *6*, 1877–1894, and references therein.

[8] a) E. Palomares, M. V. Martínez-Díaz, S. A. Haque, T. Torres, J. R. Durrant, *Chem. Commun.* **2004**, 2112–2113; b) P. Y. Reddy, L. Giribabu, C. Lyness, H. J. Snaith, C. Vijaykumar, M. Chandrasekharam, M. Lakshmikantam, J.-H. Yum, K. Kalyanasundaram, M. Grätzel, M. K. Nazeeruddin, *Angew. Chem.* **2007**, *119*, 377–380; *Angew. Chem. Int. Ed.* **2007**, *46*, 373–376; c) A. Morandeira, I. López-Duarte, M. V. Martínez-Díaz, B. O'Regan, C. Shuttle, N. A. Haji-Zainulabidin, T. Torres, E. Palomares, J. R. Durrant, *J. Am. Chem. Soc.* **2007**, *129*, 9250–9251; d) J.-J. Cid, J.-H. Yum, S.-R. Jang, M. K. Nazeeruddin, E. Martinez-Ferrero, E. Palomares, J. Ko, M. Graetzel, T. Torres, *Angew. Chem.* **2007**, *119*, 8510–8514; *Angew. Chem. Int. Ed.* **2007**, *46*, 8358–8362; e) P. A. Troshin, R. Knoeppe, A. S. Peregudov, S. M. Peregudova, M. Egginger, R. N. Lyubovskaya, N. S. Sariciftci, *Chem. Mater.* **2007**, *19*, 5363–5372.

[9] F. R. Li, S. I. Yang, Y. Z. Ciringh, J. Seth, C. H. Martin, D. L. Singh, D. H. Kim, R. R. Birge, D. F. Bocian, D. Holten, J. S. Lindsey, *J. Am. Chem. Soc.* **1998**, *120*, 10001–10017.

[10] D. Gonzalez-Rodriguez, C. G. Claessens, T. Torres, S. G. Liu, L. Echegoyen, N. Vila, S. Nonell, *Chem. Eur. J.* **2005**, *11*, 3881–3893.

[11] A. Loudet, K. Burgess, *Chem. Rev.* **2007**, *107*, 4891–4932.

[12] a) R. Ziessel, G. Ulrich, A. Harriman, *New J. Chem.* **2007**, *31*, 496–501; b) G. Ulrich, R. Ziessel, A. Harriman, *Angew. Chem.* **2008**, *120*, 1202–1219; *Angew. Chem. Int. Ed.* **2008**, *47*, 1184–1201.

[13] a) M. Koepf, A. Trabolsi, M. Elhabiri, J. A. Wytko, D. Paul, A. M. Albrecht-Gary, J. Weiss, *Org. Lett.* **2005**, *7*, 1279–1282; b) F. D'Souza, P. M. Smith, M. E. Zandler, A. L. McCarty, M. Itou, Y. Araki, O. Ito, *J. Am. Chem. Soc.* **2004**, *126*, 7898–7907; c) D. Holten, D. F. Bocian, J. S. Lindsey, *Acc. Chem. Res.* **2002**, *35*, 57–69.

[14] M. D. Yilmaz, O. A. Bozdemir, E. U. Akkaya, *Org. Lett.* **2006**, *8*, 2871–2873.

[15] J.-Y. Liu, H.-S. Yeung, W. Xu, X. Li, D. K. P. Ng, *Org. Lett.* **2008**, *10*, 5421–5424.

[16] J.-Y. Liu, E. A. Ermilov, B. Röder, D. K. P. Ng, *Chem. Commun.* **2009**, 1517–1519.

[17] a) A. Mateo-Alonso, C. Sooambar, M. Prato, *C. R. Chim.* **2006**, *9*, 944–951; b) F. D'Souza, O. Ito, *Coord. Chem. Rev.* **2005**, *249*, 1410–1422.

[18] a) F. T. Tat, Z. Zhou, S. MacMahon, F. Song, A. L. Rheingold, L. Echegoyen, D. I. Schuster, S. R. Wilson, *J. Org. Chem.* **2004**, *69*, 4602–4606; b) S. R. Wilson, S. MacMahon, F. T. Tat, P. D. Jarowski, D. I. Schuster, *Chem. Commun.* **2003**, *2*, 226–227; c) A. Regev, T. Galili, H. Levanon, D. I. Schuster, *J. Phys. Chem. A* **2006**, *110*, 8593–8598.

[19] a) R. Marczak, V. Sgobba, W. Kutner, S. Gadde, F. D'Souza, D. M. Guldi, *Langmuir* **2007**, *23*, 1917–1923; b) F. D'Souza, P. M. Smith, L. Rogers, M. E. Zandler, D. M. S. Islam, Y. Araki, O. Ito, *Inorg. Chem.* **2006**, *45*, 5057–5065; c) F. D'Souza, M. E. El-Khouly, S.

Gadde, A. L. McCarty, P. A. Karr, M. E. Zandler, Y. Araki, O. Ito, *J. Phys. Chem. B* **2005**, *109*, 10107–10114; d) M. E. El-Khouly, L. M. Rogers, M. E. Zandler, G. Suresh, M. Fujitsuka, O. Ito, F. D'Souza, *ChemPhysChem* **2003**, *4*, 474–481.

[20] R. W. Wagner, J. S. Lindsey, *Pure Appl. Chem.* **1996**, *68*, 1373–1380.

[21] A. Gouloumis, S. G. Liu, A. Sastre, P. Vázquez, L. Echegoyen, T. Torres, *Chem. Eur. J.* **2000**, *6*, 3600–3607.

[22] B. J. Littler, M. A. Miller, C.-H. Hung, R. W. Wagner, D. F. O'Shea, P. D. Boyle, J. S. Lindsey, *J. Org. Chem.* **1999**, *64*, 1391–1396.

[23] A related porphyrin-based system, constructed through the self-assembly of an axially coordinated imidazole-fulleropyrrolidine appended to the zinc center of a covalently linked zinc porphyrin–boron dipyrrin dyad, has been reported previously: F. D'Souza, P. M. Smith, M. E. Zandler, A. L. McCarty, M. Itou, Y. Araki, O. Ito, *J. Am. Chem. Soc.* **2004**, *126*, 7898–7907. Seminal ideas for covalently bonded triad Bodipy–ZnPor-C_{60} can be found in H. Imahori, H. Norieda, H. Yamada, Y. Nishimura, I. Yamazaki, Y. Sakata, and S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 100–110. Recently, an example of a self-assembled supramolecular triad composed of boron dipyrrin, ZnPor (Por = porphyrin), and C_{60} has been also reported: E. Maligaspe, N. V. Tkachenko, N. K. Subbaiyan, R. Chitta, M. E. Zandler, H. Lemmetyinen, F. D'Souza, *J. Phys. Chem. A* **2009**, *113*, 8478–8489.

[24] T. Da Ros, M. Prato, D. M. Guldi, M. Ruzzi, L. Pasimeni, *Chem. Eur. J.* **2001**, *7*, 816–827.

Received: September 11, 2009