Photophysical Properties of an Alkyne-Bridged Bis(zinc porphyrin)−Perylene Bis(dicarboximide) Derivative

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We report the synthesis, electrochemistry, and photophysical properties of a new donor−acceptor−donor molecule in which the *meso* carbon atoms of two zinc porphyrin (POR) units are linked through ethynylene bridges to the 1,7-positions of a central perylene-3,4:9,10-bis(dicarboximide) (PDI). In contrast to previously studied systems incorporating POR and PDI groups, this alkyne-based derivative shows evidence of through-bond electronic coupling in the ground state; the new chromophore exhibits absorption features similar to those of its constituent parts as well as lower energy features (at wavelengths up to ca. 1000 nm), presumably arising from donor−acceptor interactions. Transient absorption measurements show that excitation at several visible and near-IR wavelengths results in the formation of an excited-state species with a lifetime of 290 ps in 1% (v/v) pyridine in toluene. The absorption spectrum of this species resembles the sum of the spectra for the chemically generated radical cation and radical anion of the chromophore. The chromophore shows moderate two-photon absorption cross sections (2000−7000 GM) at photon wavelengths close to the onset of its low-energy one-photon absorption feature.

Introduction

Porphyrins (PORs) and other tetrapyrrolic macrocycles have attracted interest as sensitizers in photovoltaic cells,[1,2] hole-transporting materials,[3] two-photon absorbing dyes[4] for photodynamic therapy,[5] and chromophores for optical pulse suppression[6] because of their spectroscopic and photophysical properties. Zinc POR derivatives have two sets of absorption maxima: the Soret bands (observed at ca. 425 nm for simple D_{4h}-symmetric zinc porphyrins such as tetraphenyl zinc porphyrin) and Q-bands (at ca. 560 and 600 nm).[7] Simple perylene-3,4:9,10-bis(dicarboximide)s (PDIs) without substitution on any of the perylene positions are characterized by an absorption showing well-defined vibronic structure and a maximum at around 525 nm, efficient fluorescence, and successive reversible reductions to the corresponding mono- and dianions. PDI derivatives have been studied as fluorescent probes,[8,9] electron-transport materials,[10,11] electron acceptors in conjugated donor−acceptor systems for light-harvesting chromophores,[12,13] sensitizers for photovoltaics,[14] and two-photon absorbing dyes.[15−18]

The photophysical properties of several chromophores containing both POR donors (D's) and PDI acceptors (A's) have previously been reported,[19−24] with photoinduced D to A electron transfer being studied in some examples. Regardless of whether the POR units are covalently linked through the nitrogen atoms or the 1,7-positions (as in the compounds in Figure 1) of the PDI, the ground-state absorption spectra of these chromophores typically exhibit no evidence for electronic coupling between POR and PDI moieties; i.e., the spectra generally resemble the sum of those of the constituent chromophores. The relatively weak coupling can be attributed to the presence of nodal planes through the imide nitrogen atoms in both the HOMO and LUMO of PDIs in the case of *N*,*N*′-linked systems,[25] or—in the case of a zinc POR−PDI D−A−D derivative (**4**, Figure 1) in which the *meso* position of the POR units and the 1,7-positions of the PDI are linked by *p*-phenylene bridges[21]—to the twist anticipated between the phenylene bridge and the donor and acceptor moieties.

The objective of the present work is to examine the effect of stronger electronic coupling between POR and PDI moieties, achieved through the incorporation of a different conjugated linker group, namely, ethynylene groups in the new chromophore **1** (synthesized as shown in Scheme 1; see details in the Supporting Information), in place of the phenylene groups of **4**, on the photophysical properties of D−A−D chromophores. In particular, we compare the linear and transient absorption spectra of **1** to those of previously reported related compounds **4** and **5**, the latter being the only other reported compound in which the 1,7-positions of a PDI are linked through ethynylene bridges to macrocyclic donors (specifically to the 2-positions of zinc phthalocyanines, Pc's).[26] Since extended conjugated architectures of zinc POR derivatives have been reported to exhibit very large two-photon absorption (2PA) cross sections,[4]

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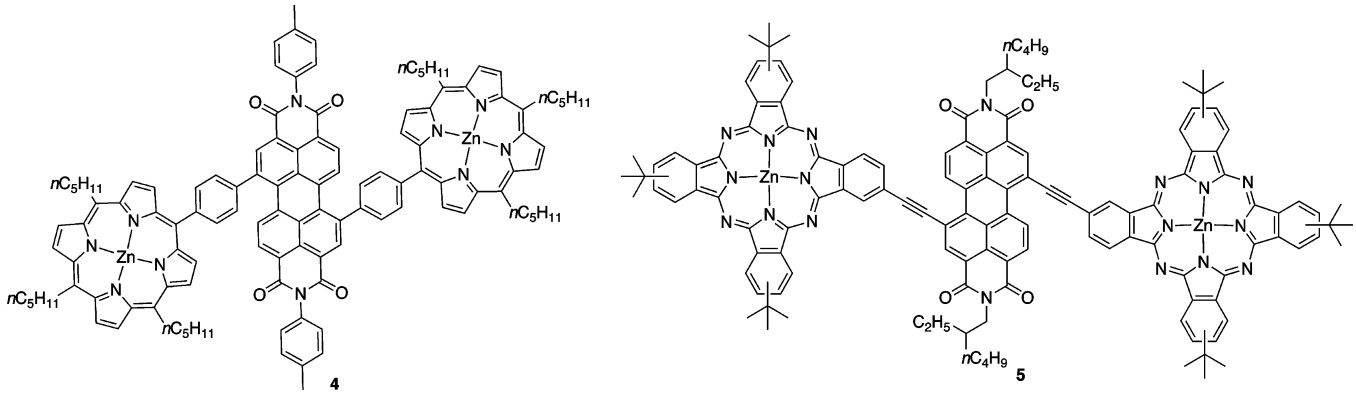
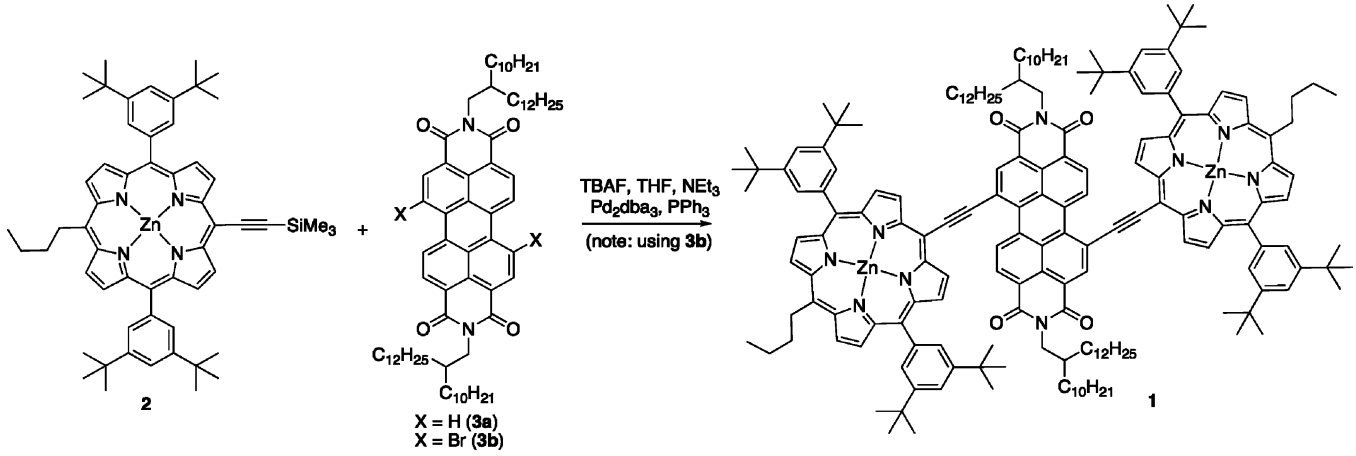


Figure 1. Previously studied compounds whose photophysical properties we compare to those of the new chromophore **1**: a phenylene-linked POR−PDI−POR chromophore[21] (**4**, left) and an alkyne-linked Pc−PDI−Pc chromophore (**5**, right).[26]

SCHEME 1: Synthesis of Alkyne-Linked POR−PDI−POR (1) Using in Situ Alkyne Deprotection and Sonogashira Coupling[a]



[a] **3b** is used as a 3:1 ratio of the 1,7-isomer (shown) and the 1,6-isomer, but **1** is obtained isomerically pure after chromatography.

which are of interest for applications including fluorescence imaging,[27] microfabrication,[28] and optical pulse suppression,[29] we have also investigated the 2PA properties of **1** in the vicinity of the one-photon absorption edge. These photophysical studies are further supplemented by electrochemical and quantum-chemical studies.

Results and Discussion

Molecular Structure and Frontier Orbitals. The DFT calculations for both **1** and **4** indicate that there are two low-energy conformers for each compound (one of which is similar to the conformation previously observed in a disubstituted PDI derivative[11]) differing in energy from one another by 0.08−0.18 eV.[30] DFT calculations (see the Supporting Information for complete details) suggest that the frontier molecular orbitals of **4** are localized on either POR or PDI units (with the HOMO and LUMO being POR- and PDI-based, respectively) with little evidence for any significant donor−acceptor interaction (see Figures 2 and 3). In contrast, compound **1** shows effective conjugation between the POR and PDI units, with both the HOMO and LUMO exhibiting significantly mixed POR/PDI character, although the HOMO retains more POR character and the LUMO more PDI character, consistent with the primarily donor and acceptor character of these respective moieties. The conjugation between POR and PDI in **1** suggests the possibility of a direct low-energy HOMO-to-LUMO optical transition for **1**, since there is significant spatial overlap between the relevant orbitals. On the other hand, this is not the case for **4**, in which the nature of the MOs suggests that the transitions are likely to be strongly localized on either POR or PDI.

Linear Absorption Spectra. The UV−vis−NIR absorption spectrum for compound **1** is compared to those of its constituent units—model compounds **2** and **3**—in Figure 4.[31] Pyridine (1%, v/v) was used to prevent aggregation of the POR moieties. The UV−vis absorption spectrum of **4**[21] is essentially the sum of individual POR and PDI absorption spectra. However, although the absorption spectrum of **1** shows a strong POR-like absorption at ca. 430 nm, the lower energy features in the 470−630 nm range are less clearly identifiable as PDI-based and POR Q-band absorptions than those observed in compound **4**. Moreover, a relatively strong feature in the NIR region, at lower energy than the absorptions of any of the building blocks, may be attributable to an interaction between the donor and acceptor moieties. The spectrum of **1** can also be compared with those of other ethynyl-substituted PDIs. That of **5**[26] is consistent with the superposition of Pc-based absorptions and the absorption bands expected for a PDI chromophore with extended conjugation, possibly also in combination with additional low-energy transitions, although a well-separated charge-transfer band is not clearly distinct from the Pc-based transitions. For 1,7-bis(arylethynyl)-PDI derivatives, weak donor and acceptor aryl groups lead to red-shifted absorptions retaining some vibronic structure, while stronger π-donating aminoaryl donors lead to structureless charge-transfer-type absorption bands.[32] The differences between **1** and **4** likely result from increased donor−acceptor coupling in the alkyne-bridged species relative to the phenylene-bridged species.

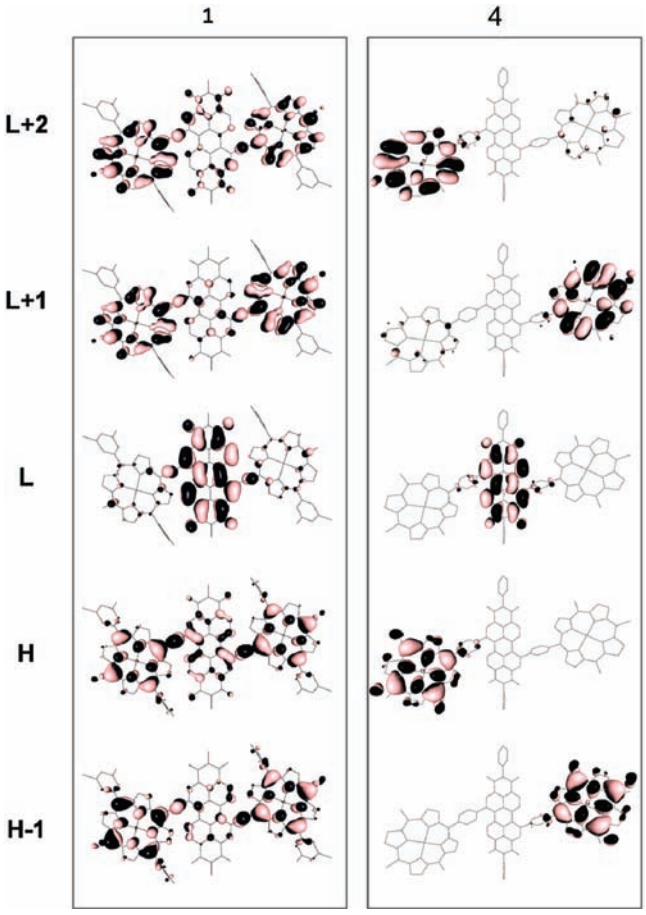


Figure 2. Illustration of the DFT wave functions for the frontier orbitals HOMO − 1 through LUMO + 2 for compounds **1** and **4**.

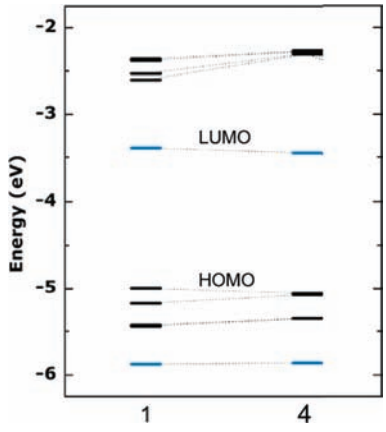


Figure 3. Molecular orbital energies for **1** and **4** computed at the B3LYP/6-31G** level. Orbitals are assigned to the donor and acceptor depending on whether POR or PDI makes the larger contribution, although the orbitals of **1** are more delocalized than those of **4**. Orbitals dominated by POR are shown in black, while those localized on the PDI are shown in blue.

Stronger coupling through ethynylene versus *p*-phenylene bridges has previously been observed in several other classes of compounds, for example, ferrocene/ferrocenium mixed valence species.[33,34] It also constitutes a general feature of *meso*-linked porphyrin systems due to the steric effect of the neighboring β-protons;[35,36] indeed, the case of **4**, values of about 60° are calculated for the torsion angles between the planes of the phenylene bridge and the PDI core. The lowest energy absorption maxima for all three sets of donors, acceptors, and D−A−D chromophores are shown in Table 1.

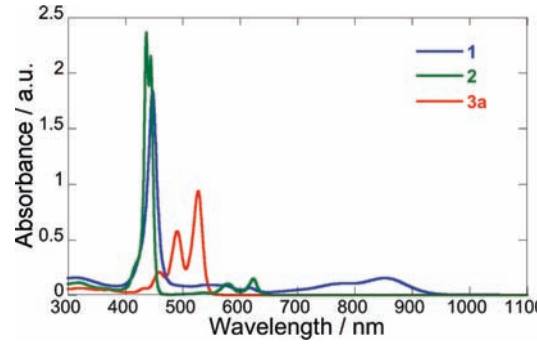


Figure 4. UV−vis−NIR absorption spectra of **1** (blue), **2** (green), and **3a** (red) in 1% pyridine in toluene.

TABLE 1: Absorption Maxima (nm) for the Lowest Energy Absorption Feature for D and A Components and for Compounds 1, 4,[21] and 5[26] in 1% Pyridine in Toluene

compd	D component	A component	D−A−D
1	623	527	852
4	614	548	613
5	681	527	716

The calculated HOMOs and LUMOs of these compounds (see above) provide some insight into the differences between the spectra of **4** and **1**. As pointed out earlier, there is little spatial overlap between the HOMO and LUMO of **4**, suggesting that a direct HOMO → LUMO excitation would have a negligible transition dipole moment; the significant spatial wave function overlap in **1** leads to the possibility of a low-energy HOMO → LUMO band with significant intensity and having some quadrupolar POR-to-PDI charge-transfer character.

The quantum-chemical calculations indicate that, in contrast to **4**, most transitions in **1** show a significant mixture of local and charge-transfer excitations. In particular, INDO calculations also predict a low-energy transition (at 716 nm), which, given the method used, is reasonably consistent with the experimental maximum of the low-energy peak. The transition is characterized by a transition dipole moment of 9.6 D, which compares very well with the experimental value of 9.7 D, estimated by integration over the range 650−950 nm in pyridine (1%, v/v) in dichloromethane. No comparable allowed low-energy transition is predicted for **4**, which is consistent with previously published experimental results.[21]

Electrochemistry. In addition to the evidence for ground-state electronic coupling between the donor and acceptor from the absorption spectra of **1**, the electrochemical potentials are also supportive of extended conjugation. Cyclic voltammetry (CV) of **1** (Figure 5) shows two one-electron oxidations and three one-electron reductions (the third reduction is not shown in Figure 5); the nonbrominated PDI model compound **3a** shows two reductions, and the model POR derivative **2** shows one oxidation and one reduction. The redox potentials are summarized in Table 2. The separation between the two oxidations of **1** suggests some interaction between the two isolated POR centers. Several factors contribute to separations between electrochemical potentials of nominally equivalent redox centers including through-space electrostatic effects, through-bond inductive effects, and electronic coupling effects.[37] The large distance between the two redox centers in **1** means that the first two contributions are likely to be minor and that the separation seen here reflects electronic coupling between the two centers; this result would be consistent with formation of a radical cation delocalized over both POR units and the bridge, consistent with the HOMO obtained from DFT calculations (Figure 2). The

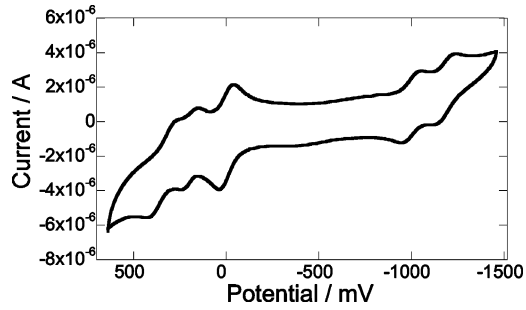


Figure 5. Cyclic voltammogram of **1** in 0.1 M $^{n}Bu_4PF_6$ in dichloromethane at 50 mV/s, shown with ferrocene as the internal reference at 0 V.

TABLE 2: Half-Wave Redox Potentials (V) of 1, 2, and 3a in 0.1 M $^{n}BuN_4PF_6$ in Dichloromethane, All Relative to $Cp_2Fe^{+/0}$ at 0 V

compd	$E_{1/2}^{2+/1+}$	$E_{1/2}^{+/0}$	$E_{1/2}^{0/-}$	$E_{1/2}^{1-/2-}$	$E_{1/2}^{2-/3-}$
1	+0.34	+0.19	−1.00	−1.19	−1.37[a]
2		+0.25	−1.73		
3a			−1.06	−1.26	

[a] Not displayed in the voltammogram in Figure 5.

result can be contrasted with 1,7-bis(arylethynyl)-PDIs with amine-containing aryl groups in which the two amine oxidations take place at experimentally indistinguishable potentials[32] and the HOMOs are more strongly donor-localized than in **1**.[38] Additionally, compound **1** is slightly easier to oxidize (by ca. 0.06 V) and to reduce (by ca. 0.06 V) than its isolated POR (**2**) and PDI (**3a**) components, which again is presumably due to the more delocalized nature of the HOMO and LUMO in **1**. The difference in the first reduction potential between the unsubstituted *N*,*N*′-dialkyl-PDI (**3a**) and the bis(porphyrin−ethynyl)PDI (**1**) is similar to differences previously seen in reduction potentials of an unsubstituted *N*,*N*′-diaryl-PDI and its bis(arylethynyl)-PDI derivatives (with both donor and acceptor aryl groups), with differences ranging from 0.04 to 0.11 V for these examples.[32]

Transient Absorption Spectra. Transient absorption spectra have been used to study charge separation in a wide range of donor-substituted perylene bis(dicarboximide) derivatives; these include many species with porphyrin donors,[19−22,24,32] including compound **4**.[21] However, only a few such studies have involved systems in which there is evidence for the coupling of donors and acceptors in the ground-state absorption spectrum,[26,32,39,40] only one of which—the study of compound **5**—involves a macrocyclic donor.[26] To examine whether a similar charge-separated state is formed in **1** and to probe its lifetime, transient absorption spectra were recorded for **1** in 1% pyridine in toluene using 120 fs pulses at 414, 600, and 832 nm. Figure 6 shows the transient absorption spectra (plotted as the difference in absorbance) obtained on excitation at 414 nm; the spectra obtained using 600 and 832 nm excitations are essentially identical. Bleaching of the POR Soret band at 450 nm is accompanied by the appearance of peaks with maxima around 475, 600, and 650 nm. In contrast to the transient spectra of **4**, those for **1** are rather broad, and the features are not clearly assignable to $POR^{\bullet+}$ and $PDI^{\bullet-}$ moieties (or to $\mathbf{2}^{\bullet+}$ and $\mathbf{3b}^{\bullet-}$ moieties; see the Supporting Information), precluding description of the state ultimately formed on excitation of **1** as a fully charge-separated $POR^{\bullet+}$−$PDI^{\bullet-}$−POR state with minimal cation−anion interaction. This is presumably related to the more delocalized orbital structure in **1**, i.e., the stronger coupling between POR and PDI units. Indeed the transient spectra

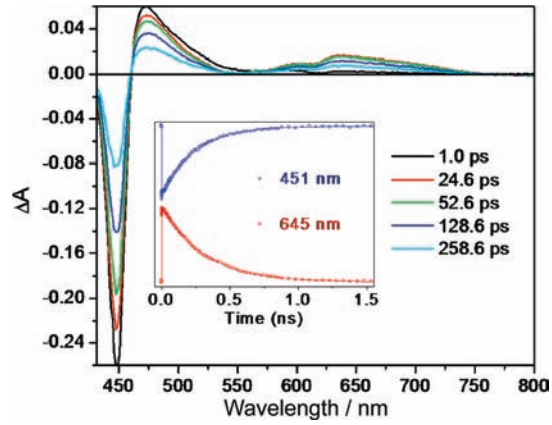


Figure 6. Transient absorption spectra of **1** in 1% pyridine in toluene, following excitation with 414 nm, 120 fs laser pulses. Inset: transient absorption kinetics for compound **1** monitored at 451 nm (blue) and 645 nm (red). Nonlinear least-squares fits to the data are also shown.

TABLE 3: Kinetics for Compounds 1, 4, and 5 from Fitting of Transient Absorption Experiments in 1% Pyridine in Toluene (PhMe)

compd, solvent	excitation wavelength (nm)	τ_R (ps)	τ_D (ps)
4, 1% pyridine in PhMe	612	10.1 ± 0.5	77 ± 3
5, 1% pyridine in PhMe	387	not provided	517 ± 52
1, 1% pyridine in PhMe[a]	414	6.5 ± 0.5	294 ± 4
1, 1% pyridine in PhMe	600	6.7 ± 0.5	291 ± 2
1, 1% pyridine in PhMe	832	6.4 ± 0.5	278 ± 8

[a] An additional feature in the kinetic fitting was observed with τ = 0.3 ± 0.1 ps, which is possibly due to the relaxation of the vertical excited state to the lowest excited state.

observed for **1** are more reminiscent of those obtained for **5**—another strongly coupled D−A−D chromophore.

Also shown in Figure 6, the transient absorption kinetics were monitored at 451 and 645 nm and were fitted using a nonlinear least-squares fit to a general sum-of-exponentials function with an added Gaussian instrument response function. The same time constants were observed following excitation at 400, 600, and 832 nm.[41] The time constants characterizing the rise and decay of the state ultimately formed by **1**, τ_R and τ_D, respectively, are compared to those for **4** and **5** in Table 3. The value of τ_R for **1** is a little lower than that for **4**, perhaps due to the increased donor−acceptor coupling. The lifetime of the state formed by **1** also falls within the range of lifetimes of species attributed to charge-separated states in other strongly coupled donor-substituted PDIs,[32,39,40] and is considerably shorter than the lifetimes of the (presumably non-charge-separated) states formed by PDIs substituted with weak π-donors or with π-acceptors.[32] In the next section the relationship between the transient spectra of **1** and the radical ion spectra is examined in more detail.

Radical Ion Spectra. As discussed above, the transient absorption spectra are not clearly interpreted as the sum of the radical ion spectra of isolated POR and PDI units. Moreover, the molecular orbitals and electrochemical data suggest that $\mathbf{1}^{\bullet+}$ is likely to be a rather delocalized species, rather than resembling an isolated $POR^{\bullet+}$ unit. Accordingly, we obtained the radical ion spectra to establish the extents to which (i) the spectrum of the state with a lifetime of ca. 290 ps observed in transient absorption experiments resembles the sum of spectra for $\mathbf{1}^{\bullet+}$ and $\mathbf{1}^{\bullet-}$ and (ii) the radical ion spectra for **1** resemble those for isolated POR and PDI units. Figure 7 shows the vis−NIR absorption spectra of **1** and the spectra obtained upon oxidation

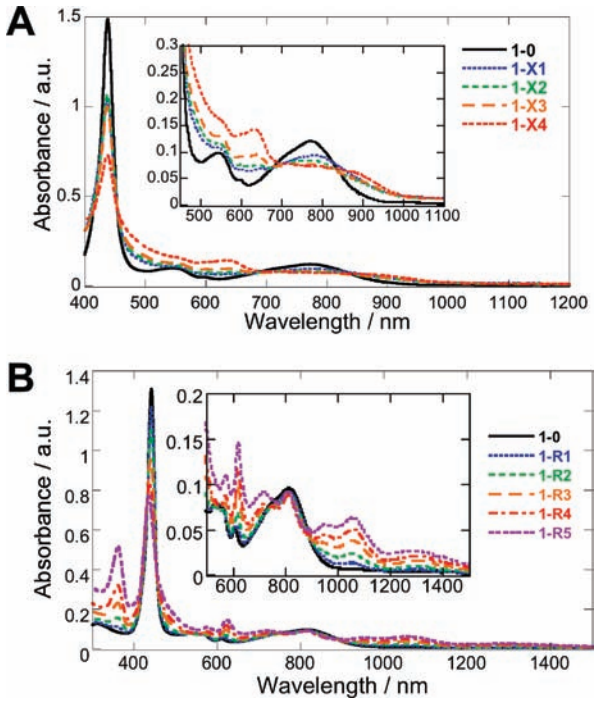


Figure 7. (A) Chemical oxidation with acetylferrocenium tetrafluoroborate in dichloromethane: 1-0 (black), neutral **1**; 1-X1 (blue) through 1-X4 (red), gradual appearance of $\mathbf{1}^{+}$. (B) Reduction with cobaltocene in THF (bottom) of compound **1**: 1-0 (black), neutral **1**; 1-R1 (blue) through 1-R5 (fuchsia), gradual appearance of $\mathbf{1}^{-}$. Insets: expansion of the region from 450 to 1100 nm (top) and from 450 to 1500 nm (bottom).

with additions of successive aliquots of acetylferrocenium tetrafluoroborate ($E_{1/2}(FcAc^{+/0}) = +0.27$ V versus $Cp_2Fe^{+/0}$)[42] in dichloromethane.[43] Chemical reduction was accomplished by addition of successive portions of cobaltocene ($E_{1/2}(CoCp_2^{+/0}) = -1.33$ V versus $Cp_2Fe^{+/0}$ in 0.1 M $^{n}Bu_4NPF_6$/dichloromethane[42]) in tetrahydrofuran to a solution of **1** in tetrahydrofuran.[44]

While the oxidation of **1** results in new features, some of which occur at energies similar to those of the absorptions of an isolated POR or ethynyl-susbtituted POR radical cation (i.e., the absorption features at ca. 640 and 890 nm, see the Supporting Information for the spectrum of oxidized **2**), it is difficult to assign the new bands to specific $POR^{\bullet+}$ features. However, some of the features associated with the bands assigned to neutral POR-based transitions have decreased in intensity. The lack of a close correspondence to a monomeric POR radical cation implies that the radical cation is not localized on a single POR moiety, consistent with the electrochemical data. Similarly, the reduction of **1** results in new peaks, some of which are at energies similar to those of PDI radical anions; 1,7-bis(arylethynyl)-PDI derivatives have been shown to have radical anion absorption features at ca. 730, 820, and 1000 nm,[32] with some variation in wavelength depending on the nature of the aryl substituent. The spectrum of the reduction of **1** shows additional peaks, such as the feature centered at ca. 1300 nm. Also, the peak assigned to the POR Soret band decreases in intensity, indicating that reduction also affects at least one of the POR moieties; this confirms that the excess electron is not restricted to the PDI ring system, consistent with minor POR contributions seen in the DFT-calculated LUMO (Figure 2).

Figure 8 compares examples of difference spectra from the transient absorption, chemical oxidation, and chemical reduction experiments. The three sets of spectra were normalized to the

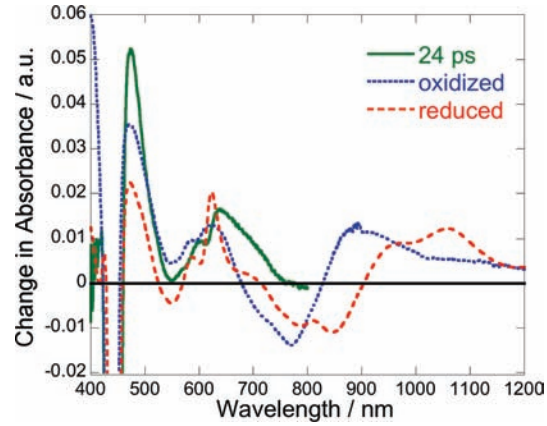


Figure 8. Transient absorption spectra of compound **1** at 24 ps in 1% pyridine in toluene following excitation with 414 nm, 120 fs laser pulses (green, solid), difference spectrum from chemical oxidation with acetylferrocenium tetrafluoroborate in dichloromethane (blue, dotted), and difference spectrum from chemical reduction with cobaltocene in tetrahydrofuran (red, dashed).

maximum of the disappearance of the Soret band of the POR at ca. 440 nm. The sum of the spectra obtained upon oxidation and reduction is not an exact match to the result from the transient absorption spectra. However, DFT results suggest delocalization of both the hole and electron over both the donor and acceptor, which would be anticipated to lead to strong hole−electron interactions in the excited state. Moreover, differences in molecular geometries and in solvation[45] between excited states and the radical ions may be expected to lead to differences in the spectra. Inevitably the stronger donor−acceptor interactions in **1** and the more delocalized character of both the radical anion and cation make the transient absorption spectra more difficult to interpret, and preclude definitive assignment of the ca. 290 ps state as a charge-separated species. However, the difference spectra broadly show that the overall changes observed in the transient absorption experiments resemble the changes observed in a combination of the chemical oxidation and reduction experiments, suggesting that the long-lived state has significant charge-transfer character.

Two-Photon Absorption. Bis-POR diynes and bis-POR diethynylarenes have previously been shown to exhibit peak 2PA cross sections into a state lying slightly higher in energy than the Soret-type band state, with cross sections up to 500 times greater than those of isolated porphyrins. These cross sections range from 3000 to 17000 GM at photon wavelengths of ca. 820−890 nm, i.e., close to the one-photon absorption edge (near double resonance with the Q-band states),[4,46,47] and have potential applications in two-photon-excited photodynamic therapy.[5] In addition, PDI derivatives and related compounds have been shown to have large 2PA cross sections at photon energies close to the one-photon edge.[15−18,32] Moreover, we have recently shown that a chromophore in which POR groups are coupled through ethynylene linkers to a bis(indolinylidenemethyl)squaraine core exhibits a 2PA spectrum that substantially differs from the sum of 2PA spectra of the constituent building blocks.[48] In view of the ethynylene-mediated donor−acceptor interactions evident in the linear spectrum of **1** and in its calculated molecular orbitals (see above), the 2PA spectrum of **1** was investigated, both theoretically and experimentally.

INDO/MRD-CI calculations of the 2PA spectrum of **1** predict the presence of 2PA active states with cross sections greater than 3500 GM at a state energy of ca. 2.58 eV due to strong coupling between POR and PDI moieties, while the lack of such

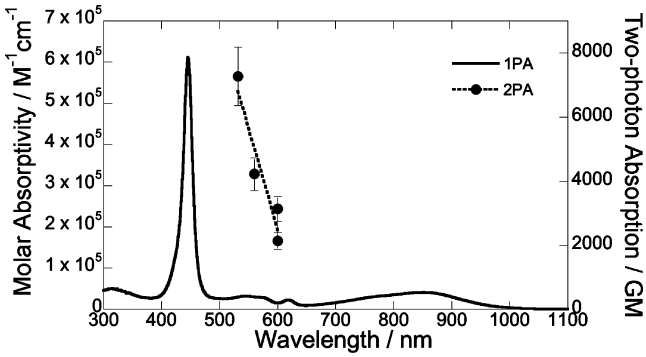


Figure 9. Two-photon absorption at 1064, 1120, and 1200 nm of compound **1** plotted versus the transition wavelength, measured by Z-scan, shown with its linear absorption spectrum, all in 1% pyridine in dichloromethane.

coupling in **4** leads to the corresponding transitions being 2PA-inactive. Thus, the POR−PDI coupling plays a crucial role in affording significant 2PA cross section at lower energies than are observed for individual POR and PDI chromophores.

2PA cross sections for compound **1** were measured using the degenerate Z-scan technique at photon wavelengths of 1064, 1120, and 1200 nm (Figure 9); for consistency with previously measured POR monomers and dimers,[4] the solvent chosen for 2PA measurements was 1% pyridine in dichloromethane. The 2PA cross sections range from 2100 to 7000 GM, with the largest error bar at 1064 nm, close to the onset of the linear absorption and where contributions from ESA (both 2PA- and 1PA-induced, with ESA leading to reverse saturable absorption) could not be ruled out. The measured 2PA cross sections are on the same order of magnitude as those of other POR dimer and PDI derivatives, although the observable 2PA state occurs at lower energy for compound **1** than for previous POR and PDI systems (with the exception of our previously reported porphyrin−squaraine chromophore[48]). In particular, strong 2PA is observed in **1** at lower energy than the Soret-type state, while in previously studied POR dimers, the strongly 2PA-allowed state lies higher in energy than the Soret-type state, which presumably implies that a different type of state is involved. Thus, the incorporation of PDI into a conjugated bis-POR architecture enables the tuning of the 2PA absorption of POR derivatives into the near-IR.

Conclusions

In conclusion, we have synthesized an ethynylene-linked D−A−D derivative, **1**, with ethynylene-linked POR and PDI moieties; to the best of our knowledge this is first example of a photophysical study of a strongly coupled POR−PDI chromophore.[49] In contrast to that of a related *p*-phenylene-bridged system, **4**, the UV−vis−NIR absorption spectrum of **1** deviates significantly from the sum of spectra of isolated POR and PDI units, demonstrating more extensive donor−acceptor interaction. This finding is consistent with quantum-chemical calculations showing more extensive delocalization of frontier orbitals over both the donor and acceptor, and with electrochemical data. Transient absorption spectra show that a state with a lifetime of ca. 290 ps is formed on a ca. 6 ps time scale following photoexcitations at multiple wavelengths in the vis−NIR region; the lifetime of this state is slightly longer than that of the state formed by its *p*-phenylene analogue,[21] but shorter than that in an alkyne-bridged Pc−PDI−Pc system.[26] The spectrum of the excited state with a lifetime of 290 ps is qualitatively different from that of the state ultimately formed by its phenylene analogue, which closely resembles the sum of the spectra of localized POR and PDI radical ions. However, similarities of the transient spectrum of **1** to the spectra of the chemically generated radical cations and anions suggest significant charge-transfer character to this excited state. Large 2PA cross sections are found for **1** at wavelengths of ca. 1.06−1.20 μm, at which isolated POR and PDI chromophores do not absorb. Quantum-chemical calculations indicate that this 2PA can be attributed to the presence of frontier molecular orbitals with mixed POR and PDI character and that comparably long-wavelength strong 2PA is not expected for the more weakly coupled compound **4**. In summary, the differences in photophysical properties between phenylene- and alkyne-based D−A−D derivatives can be understood in terms of greater electronic coupling between D and A moieties, which can allow for tuning of the optical properties for different potential applications.

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Supporting Information Available: Experimental details, synthetic details, additional UV−vis absorption spectra of chemically oxidized and reduced model compounds, and additional transient absorption spectra. This information is available free of charge via the Internet at http://pubs.acs.org.

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