

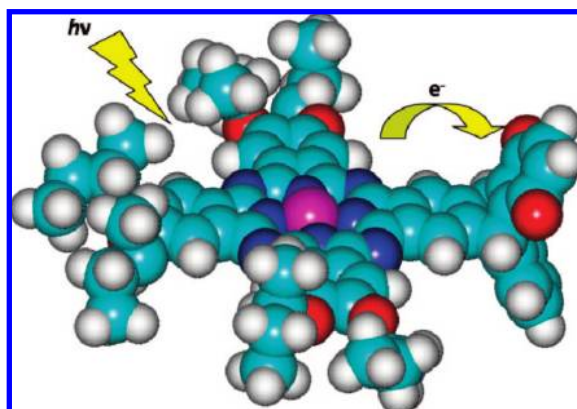
Novel Zinc Phthalocyanine-Benzoquinone Rigid Dyad and Its Photoinduced Electron Transfer Properties

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While preparing the first structurally rigid zinc phthalocyanine-benzoquinone (ZnPc-BQ) dyad as a model for photoinduced charge separation mimicking natural photosynthesis, a convenient method is developed for in situ generation of a benzoquinone chromophore in the dyad using an *iso*-butyryl mask. The dyad has no rotamers and possesses a fixed distance between ZnPc and BQ moieties (center-to-center and edge-to-edge distances are 9.40 and 2.14 Å, respectively). The dyad displays unusual electronic perturbation in the ground state, resulting from the interactions between Pc and BQ, and exhibits photoinduced electron transfer with a lifetime of 40 ps of the charged separated states. The steady-state fluorescence and electrochemical behavior of the dyad are evaluated. This study opens a route to subsequent dyads, triads, and complex architectures of electron donor–acceptor arrays with rigid structures and long charge separation states.

Introduction

In natural photosynthesis, the primary energy conversion reactions involve efficient sequential photoinduced electron transfer (PET) steps that result in charge separation across a biological membrane. Thus, light is converted into an electrochemical potential that provides ammunition for the biosynthesis of high-energy biological fuels, such as adenosine triphosphate (ATP).^{1,2} In natural bacterial photosynthetic systems, the initial PET occurs from a bacterial chlorophyll (BChl) dimer to a bacterial pheophytin (Bph) and then to two quinone derivatives,

Q_A and Q_B.³ These chromophores are not covalently linked but are “vitrified” in suitably close proximity by protein scaffolds. A key strategy for mimicking natural photosynthesis or the construction of synthetic solar energy conversion systems is by

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employing multistep PET among suitable chromophores with optimal redox potentials, optimized electron donor (D) and acceptor (A) orientation, distance, and environment. The most attractive laboratory approach in synthesizing artificial photosynthetic systems has been by linking appropriate D and A moieties with covalent bonds, instead of using proteins.

Phthalocyanines (Pc) and porphyrins (Por) have been used as electron donor building blocks in artificial photosynthetic systems due to their strong absorption in the solar spectrum for light harvesting, their redox potentials enabling PET, and their structural tunability by chemical synthesis. Also, benzoquinone (BQ), perylenediimide (PDI), and C₆₀ are a few of the most commonly used electron acceptors. While a variety of electron D-A dyads (e.g., Por-BQ,^{4–7} Pc-BQ,⁸ Por-C₆₀,⁹ Pc-C₆₀,^{10–13} Por-PDI,¹⁴ Pc-PDI¹⁵) and a few triads^{11a,16} (such as β -carotenoid-Por-C₆₀ and C₆₀-Pc-C₆₀) have been synthesized and studied for generating and sustaining long-lived charge-separated states, the correlation between the PET efficiencies and structural factors may not be clearly established as a result of the coexistence of conformers as a result of structural flexibility in

these synthetic systems. Most dyads and triads prepared involving Pc, Por, and Chl (chlorophylls) blocks thus far lack molecular structural rigidity (i.e., variation in center-to-center distance (r_{DA}) or the relative orientation between D and A). Hence, dynamic structural factors need to be considered in order to accurately establish the structural factor dependency of PET, which often is not straightforward. Therefore, it is necessary to construct structurally rigid D–A systems (only one conformer), which will offer the opportunity to deconvolute the multiple structural influence in PET and allows optimization of intended structural variables for PET processes. In light of this awareness, we initiated a research program in developing rigid metallophthalocyanine-benzoquinone (MPC-BQ)-based dyads with varied D–A distances and orientations. The goal of this research is to obtain a reaction coordinate where these chromophores provide the highest PET efficiency.

We have chosen ZnPc as an effective donor owing to its optical absorption characteristics that are very similar to those

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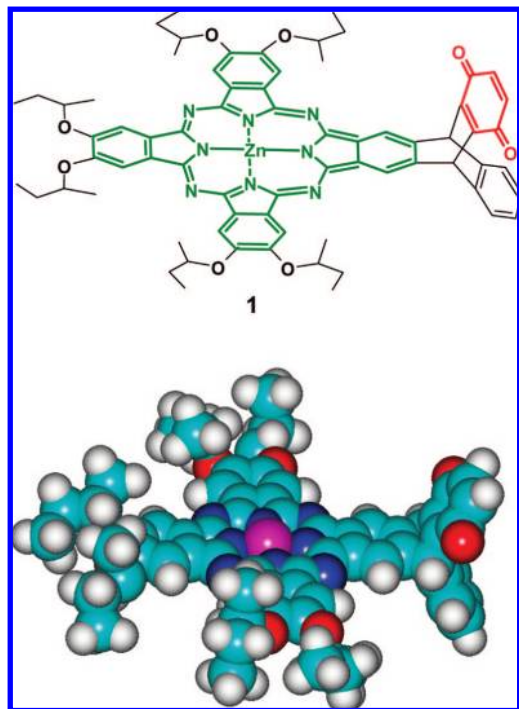


FIGURE 1. Structure of **1** (below is the space-filled model).

of chlorophylls and outstanding thermal and chemical stability, including much simpler synthetic protocols compared with chlorophyll. Similar to the natural systems, BQ remained our choice as the preferred acceptor. It is important to note that although a few rigid dyads¹⁸ (some of them synthesized for different studies) have been described, the preparation of MPC-BQ-based “rigid dyads” has not yet been reported.

In this paper, we elucidate the synthesis and photophysical properties of the first member of a new class of a highly rigid D-A dyad, **1**, by annulating ZnPc and BQ into an “iptycene” scaffold (Figure 1). This system **1** consists of multiple rigid covalent bonds to “lock” the distance and orientation of benzoquinone relative to the metal center of the phthalocyanine. The center-to-center and edge-to-edge distances between ZnPc and BQ have been determined by an energy minimized structure (calculated by Hyperchem 7.0 from Hypercube) at 9.40 and 2.14 Å, respectively. The angle between the planes of ZnPc and BQ is estimated near 120°.

Results and Discussion

Dyad Synthesis. The preparation of triptycene-fused phthalocyanines by Luk'yanets et al.¹⁹ dates back to 1972. However, the construction of rigid artificial photosynthetic systems by forging phthalocyanine and benzoquinone around a triptycene framework has, until now, not been explored. The synthesis of the substituted ZnPc-BQ dyad (**1**) was accomplished after

conducting a series of approaches (Schemes 1–4). An ideal strategy to synthesize **1** would be by direct cyclotetramerization of **3** with **5** (an oxidized form of **4a**) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and zinc acetate in 1-pentanol. Unfortunately, our initial attempts to obtain **5** by one-pot demethylation and oxidation of **4a** with ceric ammonium nitrate (CAN) were unsuccessful (vide infra). Attempts to demethylate **4a** with BBr₃ to form **6** were also fruitless, which derailed our plan for subsequent oxidation with dichlorodicyanoquinone (DDQ) to obtain **5**. It appears that the nitrile group is very sensitive toward these reagents. We then devised an alternate strategy involving the preparation of a *p*-dimethoxybenzene-fused phthalocyanine precursor (**2a**), a masked quinone of **1**.

As depicted in Scheme 1, cyclotetramerization of **3** with a *p*-dimethoxybenzene-fused triptycene derivative (**4a**) provided the desired low-symmetric phthalocyanine, **2a**, which was easily separated from other undesired statistical analogs using a silica gel column with 2:1 hexane–ethyl acetate as the starting eluent, with gradual increase in ethyl acetate proportion. In order to increase the yield of **2a**, an excess molar ratio of **3** was essential, which also produced octa-substituted alkoxy phthalocyanine (**7**) as the major product but was easily separable from **2a** by column chromatography. Although CAN in aqueous acetonitrile has been widely used as a reagent for converting the *p*-dimethoxybenzene moiety to *p*-benzoquinone,²⁰ this method was ineffective for this phthalocyanine system. Treatment of **2a** with CAN led to an ill-defined mixture of products with degradation of the phthalocyanine ring, as revealed by the loss of the Q-band in UV–vis spectrometry. Treatment of **2a** with BBr₃ also led to a mixture of uncharacterizable products due to cleavage of the *sec*-butoxy groups. Consequently, another quinone-masked phthalonitrile derivative, **4b**, was prepared to address the issue of deprotection and oxidation.

The synthesis of quinone-masked phthalonitrile analogs **4a** and **4b** was accomplished by starting with previously reported compounds 1,4-dimethoxyanthracene (**8**)²¹ and 1,4-dibenzoyloxyanthracene (**9**)^{21b} respectively (Scheme 2). Diels–Alder reaction of these compounds with 1,2,4,5-tetrabromobenzene (via in situ benzyne formation) afforded the corresponding dibromotriptycenes (**10** and **11**), which were conveniently cyanated via the Rosenmund–von Braun reaction to give the phthalonitrile analogs (**4a** and **4b**) in good yields. As mentioned earlier, we have not yet been successful in preparing the desired quinone (**5**), which could be used to synthesize **1** by direct cyclotetramerization with **3**. Moreover, it should be noted that there is no literature precedence pertaining to the cyclotetramerization of phthalonitriles in the presence of a quinone moiety, and we are uncertain whether **1** can be prepared by reaction of **3** with **5**, since there is concern about possible side reactions of quinone under cyclotetramerization conditions. To address this issue, alternative deprotection strategies using pyridinium hydrochloride for **4a** and benzyl deprotection by hydrogenolysis

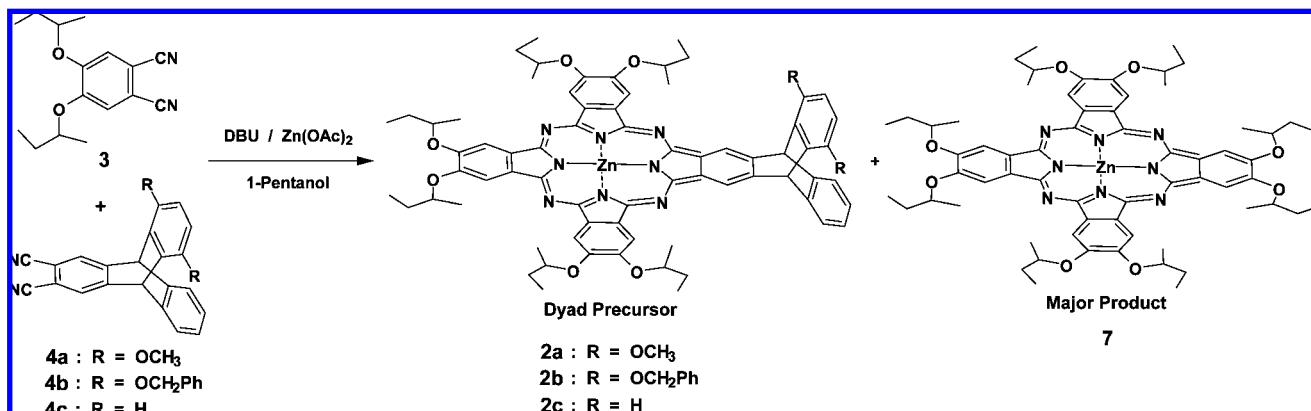
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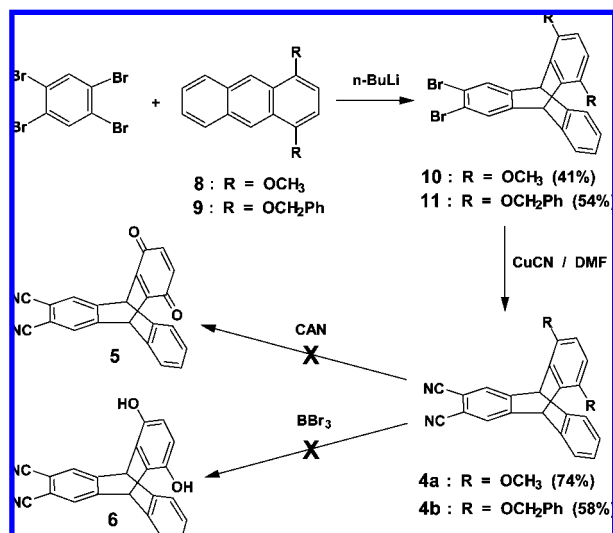
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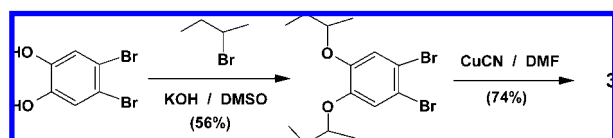
SCHEME 1. Synthesis of PcZn-BQ Dyad Precursors



SCHEME 2. Synthesis of Quinone-Masked Phthalonitrile Analogs



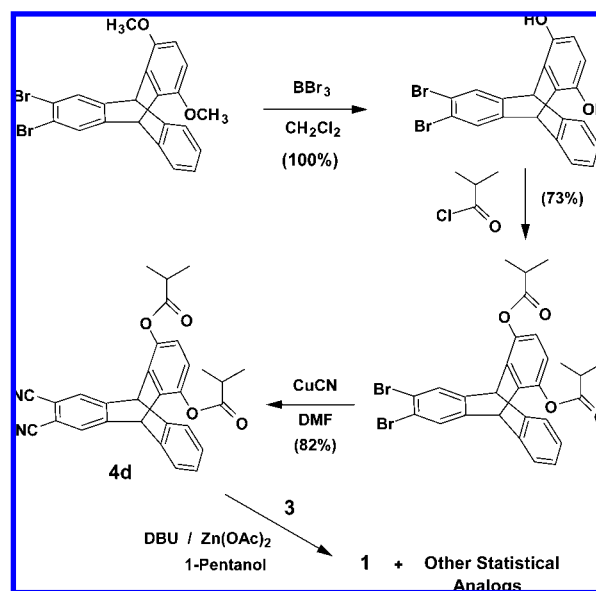
SCHEME 3. Synthesis of Phthalonitrile Derivative 3



of **4b**, including a follow-up DDQ oxidation step, are in progress. While there is uncertainty about cyclotramerization of **5** with **3**, we have successfully prepared the benzyl-masked dyad precursor, **2b**. Benzyl masking, which involves very mild deprotection conditions (palladium-catalyzed hydrogenolysis), was chosen to preserve the alkoxyl groups on the peripheral sites of the phthalocyanine ring. However, poor solubility of **2b** in ethanol (common solvent for catalytic hydrogenation) deprived us of complete removal of benzyl groups from **2b**. The use of other solvent systems, which dissolve **2b**, such as THF and dioxane, also did not provide completely deprotected hydroquinone product.

The phthalonitrile derivative, **3**, a new compound, was prepared according to the strategy outlined in Scheme 3. There are several reasons for the selection of the *sec*-butyloxy group. In addition to improved solubility of the resulting phthalocyanine, *sec*-butyloxy groups prevent aggregation, a common

SCHEME 4. Synthesis of ZnPc-BQ Dyad 1



property of phthalocyanines bearing linear alkyl chains.²² An aggregation-free phthalocyanine system is desirable to obtain accurate photophysical properties of the dyad. Our studies concluded that the *sec*-butyloxy group provides a higher yield (45%) compared to yields using longer branched or bulky alkanes (e.g., 10% for the *iso*-pentyloxy group with monosubstitution as the major product, caused by more steric crowding).

While searching for a suitable masking system, we discovered that the *iso*-butyryl group provides a solution to prepare the coveted rigid dyad **1**, without the need for deprotection or an oxidation step. The *iso*-butyryl masked dinitrile compound **4d** was prepared according to the protocol outlined in Scheme 4. The *iso*-butyryl group was found very resistive to the cyanation reaction conditions as we obtained **4d** in 82% yield. However, deprotection occurs very slowly via trans-esterification under

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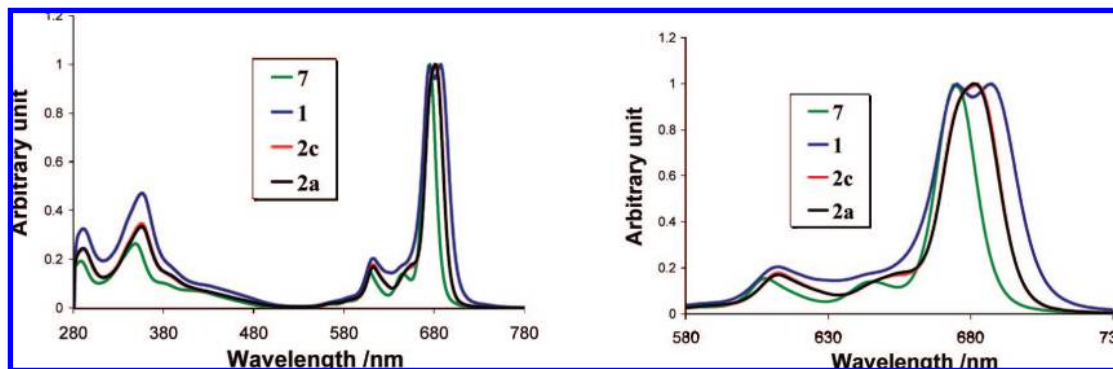


FIGURE 2. UV-vis spectra of **1**, **2a**, **2c**, and **7** in toluene (left, overall; right, focus on the Q-bands).

the conditions of cyclotetramerization (DBU in refluxing 1-pentanol) but does not interfere with the mechanism of the formation of phthalocyanine. The presence of excess 1-pentanol shifts the equilibrium toward the formation of *n*-pentyl *iso*-butyrate and unmasked hydroquinone intermediate,²³ which we believe slowly undergoes air oxidation to **1** over a period of time. Thus, this one-pot reaction involving cyclotetramerization of dinitrile derivatives, cleavage of *iso*-butyryl groups, and self-oxidation of the hydroquinone moiety to quinone is the highlight of the present work, which provides easy access to a new class of D-A molecules. The structure of **1** was confirmed by FTIR (sharp quinone carbonyl peak at 1655 cm⁻¹), ¹H NMR, ¹³C NMR (carbonyl carbon at 183.7 ppm), and mass spectrometry ($M^+ = 1216.7$).

Ground-State Absorption Properties. Figure 2 shows the UV-vis absorption spectra of **1** as well as three relevant reference compounds, **2a**, **2c** (low symmetric triptycenophthalocyanine), and **7** (symmetric Pc generated from **3**). Interestingly, **1** showed splitting of the Q-band into a doublet (peaks at 675 and 688 nm) compared to the singlet for **2a** (682 nm), **2c** (682 nm), and **7** (675 nm). Such a phenomenon has been observed previously in other asymmetric substituted Pc derivatives²⁴ and has been attributed to the perturbation from the substituted group (i.e., the linked benzoquinone)²⁵ or simply the change in the Pc symmetry from D_{4h} (**7**) or C_{2v} (**2c**) to C_s (**2a**, **1**), breaking the molecular orbital degeneracy with respect to *x* and *y* axes that aligned with two orthogonal N-Zn-N directions in the Pc plane. When we compare the spectra of **2a**, **2c** with **1**, it is clear that the symmetry change alone is insufficient to cause the Q-band splitting.^{10g,26} Although all compounds are asymmetric, the splitting of the Q-band only occurs in the latter when the BQ moiety is present. Consequently, the doublet in **1** is mostly likely due to the perturbation of the BQ to the electronic structure of the ground-state Pc core. Such interference is common in the triptycene system with aromatic substituents involving π -conjugated systems with double/triplet bond linkages²⁷ or NO₂ groups.²⁸ This perturbation also causes progressive red shifts of both Soret and Q-bands from **7** to **2c** and then to **1**.

Aggregation Properties. Most Pc derivatives have strong tendencies to form aggregates via π - π stacking, forming H-aggregate-like assemblies.²² Hence, the spectra in the Q-band region will have blue shifts and an overall broadening of the absorption peak. We have confirmed that **1** does not aggregate since a plot of the Q-band intensity against the sample concentration at selected absorption wavelengths displays linear correlation between the two, following Beer-Lambert's Law.²⁹

Steady-State Fluorescence Properties. Comparison of the steady-state fluorescence spectra of **1** with the reference compound **2c** indicates significant fluorescence quenching due to the presence of the BQ moiety that could prompt the PET process. As seen in Figure 3, the fluorescence of ZnPc in **2c** has been reduced by a factor of 8.7 in THF and of 5.8 in toluene, respectively, due to the presence of the acceptor BQ, corresponding to 88% and 82% quenching of the fluorescence. Hence, only 12% and 18% excited-state population decays through channels other than PET, such as internal conversion to the ground state and the intersystem crossing to the triplet state whose lower energy compared to that of the singlet excited state may not provide sufficient driving force for the PET reaction. In addition, the fluorescence quenching ratio of the D-A differs in THF and toluene, with the latter showing less quenching as expected for the PET reaction being promoted by the polar

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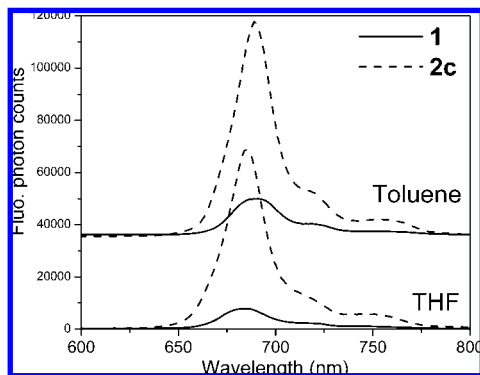


FIGURE 3. Steady-state fluorescence spectra of **1** and **2c** (normalized with the same optical density at the excitation wavelength 365 nm). In order to have the same (0, 0) band intensity, the fluorescence of **1** must be multiplied by a factor of 8.7 in THF and 8.2 in toluene, corresponding to the fluorescence quenching in the two solvents as 88% and 82%, respectively.

TABLE 1. Comparison of Electrochemical Properties of **1** with Reference Compounds

	reduction		oxidation	
	second	first	first	second
Zn(obxPc)	−1.47	−1.05	0.54	
7	−1.43	−1.08	0.43	1.09
2c	−1.49	−1.16	0.41	1.07
1	−1.86	−1.36 (−0.49)	0.46	1.05
ferrocene			0.45	
quinone	−1.08	−0.33		

solvent to gain the driving force from reorganization energy of the solvent molecules.

Electrochemical Properties. The electrochemical properties of **1**, **2c**, and **7** were examined, and the results are summarized in Table 1. The cyclic voltammogram (CV) of **7** shows two irreversible one-electron oxidations (0.43 and 1.09 V) and two quasi-reversible reductions (−1.08 and −1.43 V). These values match those of the reported isomeric compound, 2,3,9,10,16,17,23,24-octa(*n*-butyloxy)phthalocyaninato zinc(II)[Zn(obxPc)],³⁰ which have all *n*-butyloxy substituents.

The redox potential of **2c** is also in the same range as for **7**. The first ring oxidation is separated from the first ring reduction by ~1.5 V, suggesting that the energy difference between the HOMO and LUMO of the macrocyclic ring is not affected by the triptyceno linkage.³¹ In other words, the interaction between the iptyceno phenyl ring and the phthalocyanine macrocycle is insignificant.

In general, Pc derivatives show two irreversible one-electron oxidations and up to four quasi-reversible reductions and do not have redox peaks in the 0 to −0.5 V range. Comparing CVs of **7** and **2c** with that of **1** shows similarities in the oxidation reactions with two irreversible oxidation potentials (at 0.46 and 1.05 V) for the latter. However, the reduction potentials are shifted toward more negative values, from −1.1 to −1.4 V for the first reduction and from −1.5 to −1.9 V for the second reduction. A closer look at the CV curve of **1** revealed a redox couple near 0.49 V (Figure 4). This is attributed to the presence of BQ (with its first reduction ~0.34 V) and its influence on the redox potential of Pc through the iptyceno phenyl ring. Thus,

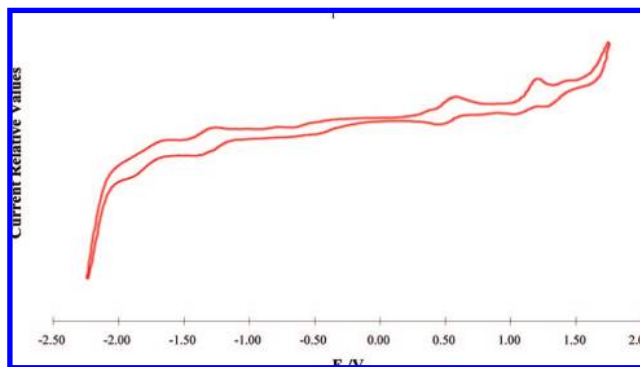


FIGURE 4. Cyclic voltammogram of **1**.

this observation also supports the long-range electronic interactions between the Pc macrocycle and BQ as inferred from UV–vis spectrometry.

The redox potentials, in particular the 0-0 transition energy for the Pc donor, and the oxidation and reduction potentials of the ground-state donor and acceptor, respectively, will allow us to estimate the driving force for the PET reaction. For the charge separation (CS) process, $\Delta G_{CS} = E_{ox} - E_{red} - E_{0-0} + \Delta G_d$ and the charge recombination process, $\Delta G_{CR} = -E_{ox} + E_{red} - \Delta G_d$ where the E_{ox} , E_{red} , and E_{0-0} are potentials for the oxidation potential of the donor, the reduction potential of the acceptor, and the energy of the lowest excited state from which the PET takes place. ΔG_d is the free energy by which the ion pairs are destabilized. Ignoring the Coulombic interactions, the CS state energy of the dyad can be determined from the difference between potentials (Table 1), and the energy difference between the reactant $^1\text{ZnPc}^*-Q$ and the product ZnPc^+-Q^- is ~0.8 eV, which warrants a sufficient driving force ΔG_{CS} for the PET to take place.

Kinetics of Photoinduced Electron Transfer Processes.³² As mentioned above, the 0.8 eV energy difference between the reactant $^1\text{ZnPc}^*-BQ$ and the product ZnPc^+-BQ^- , as well as the solvent polarity dependence of the fluorescence quenching, suggest that the PET process takes place in **1**. This is further confirmed by the absorption of ZnPc^+ identified as featured absorption in the 520–550 nm region.³³ The absorption feature appears in the transient absorption (TA) spectra of **1** but not in **2c** (Figure 5a and b).

The ground-state bleaching and recovery kinetics of **1** in THF and toluene differ significantly from those of **2c** (Figure 5c), distinguished by a drastic change in the rates for the rise and recovery of the ground-state bleaching signal. When the acceptor BQ is absent, hence the PET, the rise of the ground-state bleaching of **2c** in toluene can be described by a biexponential function with time constants of 0.3 ps (88%) and 19 ps (12%), while the recovery of the ground-state bleaching signal can be described by another biexponential function with time constants of >6 ns (82%) and 117 ps (18%).

When the acceptor BQ is present in **1**, the ground-state recovery in toluene is much faster than in **2c** and can be described by a biexponential function with time constants of 40 ps (75%) and more than several nanoseconds (25%), which is beyond the time delay limit of the experimental setup. In THF, the biexponential ground-state recovery kinetics has time

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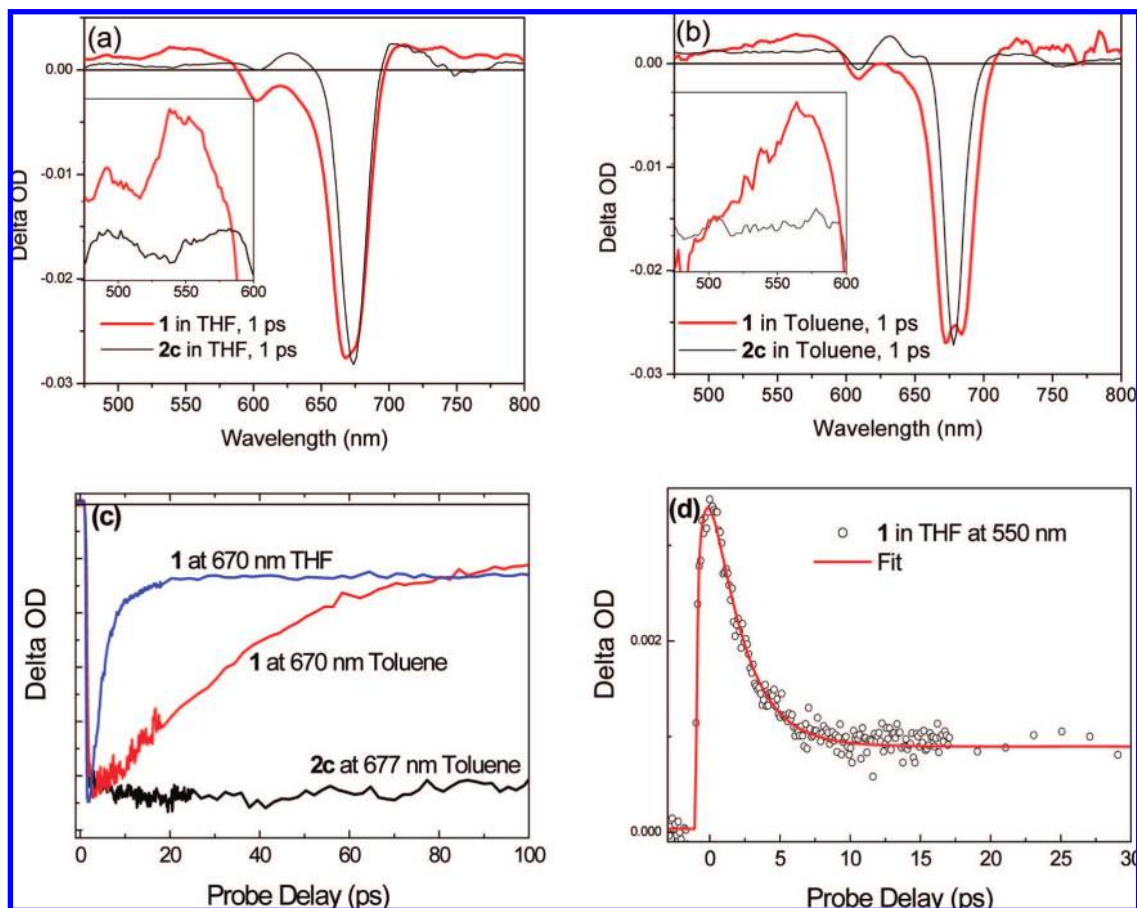


FIGURE 5. Transient absorption spectra of **1** and **2c** in (a) THF and (b) toluene at 1 ps delay, showing the differences in absorption features in the 500–600 nm region; (c) kinetics curves of **1** and **2c** monitored by the ground-state bleaching signal in toluene and THF; (d) kinetics of ZnPc⁺ in **1** monitored at 550 in THF. All measurements were made at room temperature.

constants of 3.5 ps (80%) and more than several nanoseconds (20%), which is also beyond the time delay range of the experiment. The ground-state recovery time for **1** gives an upper limit of the D⁺-A⁻ lifetime, which is as short as 2–3 ps in THF (Figure 5d) and 40 ps in toluene. The long time constant for the remaining 20–25% of the ground-state recovery signals reflects that in **2c** when the PET is absent. This result combined with the steady fluorescence quenching where there is still 15–20% unquenched fluorescence in **1**, suggests that the energy level of the triplet state (³ZnPc*) is nearly equal to or slightly lower than that of the charge separation species, ZnPc⁺-BQ⁻. Hence, the intersystem crossing competes with the PET process, which survives the 20–25% excited-state population to pathways other than PET.

Conclusion

In conclusion, we have discovered a novel method for in situ generation of the quinone moiety by using a *iso*-butyryl mask. This methodology provides access to a new generation of phthalocyanine-benzoquinone dyads. Most importantly, **1** represents one of the very few artificial photosynthetic systems, first with the Pc-BQ family, which have no rotamers and a fixed distance between D and A moieties. The preparation of a second member of this family (one more annulated benzene ring between Pc and BQ, which are separated by 11.5 Å) is in progress and is expected to provide an answer to whether the

spatial distance between the D and A species has any effect on efficiency (e.g., charge transfer state lifetimes) of this class of molecules.

Experimental Section

General Synthesis of Phthalocyanine (1, 2a–c, 7). To a stirred solution of **3** and **4a–d** in a stoichiometric ratio of about 2:3 were added zinc acetate and 1-pentanol. The solution was refluxed for 24–48 h. The product was column chromatographed with a gradient of hexane/EA from 2:1 to 1:3 and yielded different portions.

Data for 1: ¹H NMR (CDCl₃ δ = 7.26) 8.5–9.0 (br, 8H), 7.9 (br, 2H), 7.4 (br, 2H), 6.6 (br, 2H), 6.2 (br, 2H), 5.0 (br, 6H), 1.9–2.2 (br, 12H), 1.6–1.8 (m, 18H), 1.2–1.3 (m, 18H); ¹³C NMR (CDCl₃ δ = 77.0) 183.7, 154.6, 154.3, 152.8, 152.0, 151.9, 151.5, 151.4, 151.2, 143.7, 143.5, 135.9, 135.7, 135.5, 132.7, 132.1, 128.2, 126.0, 125.5, 125.2, 118.1, 110.1, 109.9, 108.7, 65.8, 48.1, 34.2, 30.3, 29.6, 29.4, 23.8, 21.2, 19.8, 19.7, 19.6, 19.4, 10.1, 10.0; IR (cm⁻¹) ν = 2967, 2933, 2877, 1655, 1606, 1488, 1459, 1401, 1381, 1346, 1275, 1217, 1188, 1091, 1040, 990, 923, 747, 730, 568, 511; [M⁺] = 1216.7; UV–vis (toluene) [λ_{max} nm (log ε)] 291 (4.71), 356 (4.87), 612 (4.51), 675 (5.20), 688 (5.20). Anal. Calcd for C₇₀H₇₀N₈O₈Zn: C (69.10) H (5.80) N (9.21). Found: C (69.05) H (5.83) N (9.27).

Data for 2a: ¹H NMR (CDCl₃ δ = 7.26) 8.3–9.2 (br, 8H), 7.9 (br, 2H), 7.4 (br, 2H), 6.6 (br, 2H), 6.4 (br, 2H), 4.8 (br, 6H), 3.9 (br, 6H), 1.9–2.2 (br, 12H), 1.6–1.8 (m, 18H), 1.2–1.3 (m, 18H); ¹³C NMR (CDCl₃ δ = 77.0) 153.5, 152.9, 152.5, 151.7, 151.5, 151.4, 149.1, 146.8, 145.7, 135.8, 135.2, 132.5, 132.2, 131.9, 125.4, 124.5, 117.6, 109.8, 109.6, 108.9, 65.5, 56.4, 48.9, 48.2, 29.6, 19.6,

10.0, 9.9; IR (cm^{-1}) ν = 3070, 2968, 2934, 2877, 2833, 1606, 1492, 1459, 1403, 1380, 1346, 1274, 1188, 1092, 1040, 987, 922, 865, 747, 730, 569; $[\text{M}^+] = 1154.8$; UV-vis (toluene) $[\lambda_{\text{max}} \text{ nm (log } \epsilon)]$ 290 (4.72), 356 (4.86), 613 (4.56), 681 (5.32). Anal. Calcd for $\text{C}_{72}\text{H}_{76}\text{N}_8\text{O}_8\text{Zn}$: C (69.36) H (6.14) N (8.99). Found: C (69.48) H (6.27) N (8.79).

Data for 2b: ^1H NMR (CDCl_3 δ = 7.26) 9.4 (br, 2H), 8.9 (br, 4H), 8.7 (br, 2H), 7.7–8.1 (t, 8H), 7.39–7.61 (dt, 10H), 5.5–5.8 (br, 4H), 5.0 (br, 6H), 1.9–2.2 (br, 12H), 1.6–1.8 (m, 18H), 1.2–1.3 (m, 18H); IR (cm^{-1}) ν = 2967, 2930, 2874, 1608, 1485, 1459, 1404, 1379, 1334, 1275, 1180, 1104, 1040, 990, 923, 746, 573, 565; $[\text{M}^+] = 1339.8$; UV-vis (toluene) $[\lambda_{\text{max}} \text{ nm (log } \epsilon)]$ 290 (4.73), 356 (4.90), 613 (4.62), 682 (5.39). Anal. Calcd for $\text{C}_{84}\text{H}_{88}\text{N}_8\text{O}_8\text{Zn}$: C (72.11) H (6.05) N (8.01). Found: C (72.35) H (6.34) N (8.17).

Data for 2c: ^1H NMR (CDCl_3 δ = 7.26) 8.74–8.78 (d, 4H), 8.00–8.40 (br, 2H), 7.60–8.00 (br, 4H), 7.20–7.40 (br, 6H), 6.70–6.90 (s, 2H), 4.80–4.90 (s, 4H), 4.30–4.60 (s, 2H), 1.80–2.20 (m, 12H), 1.30–1.80 (m, 18H), 1.10–1.30 (m, 18H); ^{13}C NMR (CDCl_3 δ = 77.0) 154.0, 153.7, 152.6, 152.0, 151.8, 151.7, 151.4, 146.0, 145.3, 135.4, 132.6, 132.2, 125.5, 124.3, 116.9, 110.2, 109.9, 109.0, 54.8, 29.7, 29.6, 29.4, 19.8, 19.7, 19.3, 15.2, 10.1, 10.0, 9.9; IR (cm^{-1}) ν = 2969, 2933, 2877, 1606, 1489, 1459, 1401, 1380, 1347, 1275, 1124, 1188, 1092, 1040, 986, 922, 746, 573, 481; $[\text{M}^+] = 1186.8$; UV-vis (toluene) $[\lambda_{\text{max}} \text{ nm (log } \epsilon)]$ 291 (4.76), 356 (4.93), 613 (4.64), 682 (5.40). Anal. Calcd for $\text{C}_{70}\text{H}_{72}\text{N}_8\text{O}_6\text{Zn}$: C (70.84) H (6.12) N (9.44). Found: C (70.92) H (6.17) N (9.49).

Data for 7: ^1H NMR (CDCl_3 δ = 7.26) 8.50–8.90 (br, 8H), 4.87–4.88 (br, 8H), 1.90–2.12 (m, 16H), 1.61–1.66 (m, 24H), 1.19–1.25 (m, 24H); ^{13}C NMR (CDCl_3 δ = 77.0) 153.0, 151.3, 132.1, 109.5, 77.6, 29.4, 27.9, 19.5, 9.9, 9.5; IR (cm^{-1}) ν = 3075, 2968, 2934, 2878, 1606, 1485, 1456, 1404, 1379, 1347, 1275, 1191, 1095, 1041, 987, 923, 889, 862, 743; $[\text{M}^+] = 1154.8$; UV-vis (toluene) $[\lambda_{\text{max}} \text{ nm (log } \epsilon)]$ 289 (4.81), 249 (4.94), 608 (4.71), 646 (4.67), 675 (5.53). Anal. Calcd for $\text{C}_{64}\text{H}_{80}\text{N}_8\text{O}_8\text{Zn}$: C (66.57) H (6.98) N (9.70). Found: C (66.41) H (7.02) N (9.81).

1,2-Dibromo-4,5-di-*sec*-butoxybenzene. To a stirred solution of 4,5-dibromobenzene-1,2-diol (48.1 g, 180 mmol) in DMSO were added KOH (94.8 g, 1.44 mol) and 2-bromobutane (93.5 g, 682 mmol). The solution was stirred at 60 °C for 3 days. The mixture was partitioned between water and CHCl_3 . The organic layer was dried under vacuum and column chromatographed with hexane to yield a colorless solution (56%). ^1H NMR (CDCl_3 δ = 7.26) 7.10–7.11 (d, J = 1.1 Hz, 2H), 4.17–4.23 (m, 2H), 1.57–1.79 (m, 4H), 1.25–1.28 (m, 6H), 0.95–1.00 (m, 6H); ^{13}C NMR (CDCl_3 δ = 77.0) 149.2, 121.8, 121.6, 115.2, 115.1, 77.7, 77.6, 29.1, 19.1, 9.7; IR (cm^{-1}) ν = 2972, 2934, 2878, 1578, 1479, 1378, 1340, 1289, 1252, 1189, 1116, 1028, 987, 916, 880, 653; $[\text{M}^+] = 380$ UV-vis (CH_2Cl_2) $[\lambda_{\text{max}} \text{ nm (log } \epsilon)]$ 296 (2.93), 237 (3.54). Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{Br}_2\text{O}_2$: C (44.24) H (5.30). Found: C (44.51) H (5.44).

4,5-Di-*sec*-butoxyphthalonitrile (3). To a stirred solution of 1,2-dibromo-4,5-di-*sec*-butoxybenzene (16.0 g, 42 mmol) in DMF (320 mL) was added CuCN (22.5 g, 252 mmol) in one portion. The solution was refluxed, and the reaction was followed by TLC until the end of the reaction. Then, the solution was cooled down after 6 h when the reaction was done. The reaction mixture was poured into 600 mL of aqueous ammonia and stirred overnight with air bubbling into the solution. The precipitate was filtered and column chromatographed with chloroform to yield a pale green solid (1.48 g, 74%). ^1H NMR (CDCl_3 δ = 7.26) 7.12–7.13 (d, J = 1.1 Hz, 2H), 4.32–4.38 (m, 2H), 1.66–1.84 (m, 4H), 1.32–1.36 (m, 6H), 0.96–1.01 (m, 6H); ^{13}C NMR (CDCl_3 δ = 77.0) 152.6, 152.5, 118.6, 118.3, 116.0, 108.2, 108.1, 77.8, 77.7, 29.0, 28.9, 19.0, 9.5; IR (cm^{-1}) ν = 3119, 3053, 2976, 299, 2882, 2227, 1764, 1585, 1518, 1466, 1402, 1384, 1359, 1290, 1228, 1213, 1125, 1087, 970, 893, 537; $[\text{M}^+] = 272$; UV-vis (CH_2Cl_2) $[\lambda_{\text{max}} \text{ nm (log } \epsilon)]$ 285 (4.05), 239 (4.61). Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_2$: C (70.56) H (7.40) N (10.29). Found: C (70.43) H (7.42) N (10.34). Mp 72–73 °C.

{5,10-[1,2]Benzeno}-7,8-dicyano-5,10-dihydro-1,4-dimethoxyanthracene (4a). To a stirred solution of 2,5-dimethoxy-8,9-dibromotriptycene (2.6 g, 5.4 mmol) in DMF (25 mL) was added CuCN (3.9 g, 43.5 mmol) was added in one portion. The solution was refluxed, and the reaction was followed by TLC. Then, the solution was cooled after 6 h when the reaction was done. The reaction mixture was poured into 300 mL of aqueous ammonia and stirred overnight with air bubbling into the solution. The precipitate was filtered and column chromatographed with CHCl_3 to yield a pale green solid (1.48 g, 74%). ^1H NMR (CDCl_3 δ = 7.26) 7.77 (s, 2H), 7.43–7.46 (dd, J = 5.7, 3.4 Hz, 2H), 7.04–7.07 (dd, J = 5.7, 3.4 Hz, 2H), 6.56 (s, 2H), 5.99 (s, 2H), 3.82 (s, 6H); ^{13}C NMR (CDCl_3 δ = 77.0) 151.9, 149.0, 143.1, 132.5, 128.0, 136.0, 124.5, 115.7, 112.7, 109.2, 56.0, 46.9; IR (cm^{-1}) ν = 3064, 2942, 2836, 2232, 1607, 1497, 1463, 1260, 1237, 1074, 795, 760, 714; $[\text{M}^+] = 364$; UV-vis (CH_2Cl_2) $[\lambda_{\text{max}} \text{ nm (log } \epsilon)]$ 217 (4.49), 264 (3.76). Anal. Calcd for $\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}_2$: C (79.11) H (4.43) N (7.69). Found: C (79.37) H (4.51) N (7.81). Mp 170–172 °C.

{5,10-[1,2]Benzeno}-1,4-dibenzyloxy-7,8-dicyano-5,10-dihydroanthracene (4b). To a stirred solution of {5,10-[1,2]benzeno}-1,4-dibenzyloxy-7,8-dibromo-5,10-dihydroanthracene (1.1 g, 1.8 mmol) in DMF (22 mL) was added CuCN (0.95 g, 10.6 mmol) in one portion. The solution was refluxed, and the reaction was followed by TLC. Then, the solution was cooled down after 6 h when the reaction was done. The reaction mixture was poured into 300 mL of aqueous ammonia and stirred overnight with air bubbling into the solution. The precipitate was filtered and column chromatographed with CHCl_3 to yield a pale green solid (0.53 g, 58%). ^1H NMR (CDCl_3 δ = 7.26) 7.92–7.94 (m, 4H), 7.77–7.80 (dd, J = 6.2, 3.3 Hz, 2H), 7.63–7.66 (d, 4H), 7.41–7.55 (m, 8H), 7.21 (s, 2H), 5.27–5.41 (m, 4H); ^{13}C NMR (CDCl_3 δ = 77.0) 150.1, 138.5, 138.0, 136.0, 131.2, 129.0, 128.1, 128.0, 126.9, 126.5, 124.6, 119.8, 115.7, 113.2, 85.3, 69.3. Anal. Calcd for $\text{C}_{36}\text{H}_{24}\text{N}_2\text{O}_2$: C (83.70) H (4.68) N (5.42). Found: C (83.92) H (4.76) N (5.61).

{5,10-[1,2]Benzeno}-7,8-dicyano-5,10-dihydroanthracene (4c). To a stirred solution of 8,9-dibromotriptycene (1.5 g, 3.6 mmol) in DMF (30 mL) was added CuCN (1.3 g, 14.6 mmol) in one portion. The solution was refluxed, and the reaction was followed by TLC. Then, the solution was cooled after 10 h when the reaction was done. The reaction mixture was poured into 200 mL of aqueous ammonia and stirred overnight with air bubbling into the solution. The precipitate was filtered and column chromatographed with CHCl_3 to yield a pale green solid (0.55 g, 50%). ^1H NMR (CDCl_3 δ = 7.26) 7.76 (s, 2H), 7.42–7.45 (dd, J = 5.4, 3.2 Hz, 4H), 7.06–7.09 (dd, J = 5.4, 3.2 Hz, 4H), 5.55 (s, 2H); ^{13}C NMR (CDCl_3 δ = 77.0) 151.3, 142.6, 128.0, 126.3, 124.3, 115.6, 113.0, 53.6; IR (cm^{-1}) ν = 3063, 3022, 2962, 2925, 2854, 2229, 1611, 1597, 1456, 1385, 1190, 1154, 1124, 1018, 970, 896, 801, 754, 628, 571, 513, 479; $[\text{M}^+] = 304$; UV-vis (CH_2Cl_2) $[\lambda_{\text{max}} \text{ nm (log } \epsilon)]$ 275 (3.09), 266 (2.82), 232 (4.03). Anal. Calcd for $\text{C}_{22}\text{H}_{12}\text{N}_2$: C (86.82) H (3.97) N (9.20). Found: C (86.90) H (4.02) N (9.33). Mp 235–238 °C.

{5,10-[1,2]Benzeno}-7,8-dibromo-5,10-dihydro-1,4-dihydroxyanthracene. To a stirred solution of {5,10-[1,2]benzeno}-7,8-dibromo-5,10-dihydro-1,4-dimethoxyanthracene (1.5 g, 3.2 mmol) in anhydrous CH_2Cl_2 (25 mL) at –78 °C was added boron tribromide (1.8 mL, 1.9 mmol) dropwise. The reaction was warmed to room temperature and stirred overnight. The reaction mixture was poured into icy water (200 mL), and ethyl acetate (50 mL) was added. The creamy yellow conglomerate formed was filtered and dissolved in an ethyl acetate/brine mixture. The organic layer was separated, dried, and column chromatographed with ethyl acetate to yield a pale brown solid (1.4 g, 100%). ^1H NMR (d -acetone δ = 2.05) 7.65 (s, 2H), 7.42–7.45 (dd, J = 5.3, 3.2 Hz, 2H), 6.99–7.02 (dd, J = 5.3, 3.2 Hz, 2H), 6.44 (s, 2H), 5.96 (s, 2H); ^{13}C NMR (d -acetone δ = 205.1) 147.1, 144.5, 144.2, 130.5, 127.8, 124.4, 123.1, 128.7, 122.7, 45.6; IR (cm^{-1}) ν = 3218, 1488, 1446, 1195, 992, 917, 884, 800, 744, 727, 643 547; $[\text{M}^+] = 444$.

Anal. Calcd for $C_{20}H_{12}Br_2O_2$: C (54.09) H (2.72). Found: C (54.15) H (2.91). Mp > 330 °C.

{5,10-[1,2]Benzeno}-7,8-dibromo-5,10-dihydroanthracene-1,4-diyl-(2-methylpropanoate). To a stirred solution of {5,10-[1,2]benzeno}-7,8-dibromo-5,10-dihydro-1,4-dihydroxyanthracene (1.4 g, 3.2 mmol) in CH_2Cl_2 (10 mL) and pyridine (1 mL) was added *iso*-butyryl chloride (1.4 mL, 13 mmol) in one portion. The reaction was stirred overnight. The reaction mixture was concentrated under vacuum and then poured into water (50 mL) and hexane (50 mL). The organic layer was separated while the aqueous layer was extracted with hexane (2 x 50 mL). The combined organic layer was dried and recrystallized in MeOH/ $CHCl_3$ to yield a pale orange product (1.3 g, 73%). 1H NMR ($CDCl_3$ δ = 7.26) 7.59 (s, 2 H), 7.32–7.35 (dd, J = 5.3, 3.2 Hz, 2H), 7.02–7.08 (dd, J = 5.4, 3.2 Hz, 2 H), 6.80 (s, 2H), 5.36 (s, 2H), 2.94–3.04 (m, 2H), 1.41–1.49 (m, 12H); ^{13}C NMR ($CDCl_3$ δ = 77.0) 183.8, 175.0, 145.2, 143.1, 143.0, 137.6, 128.9, 125.9, 124.2, 121.0, 119.9, 47.7, 34.2, 19.2; IR (cm^{-1}) ν = 3054, 2980, 2930, 1756, 1469, 1446, 1421, 1265, 1216, 1179, 1127, 1097, 896, 38, 705. $[M^+]$ = 584. Anal. Calcd for $C_{28}H_{24}Br_2O_4$: C (57.56) H (4.14). Found: C (57.62) H (4.23). Mp 149–150 °C.

{5,10-[1,2]Benzeno}-7,8-dicyano-5,10-dihydroanthracene-1,4-diyl-(2-methylpropanoate) (4d). To a stirred solution of {5,10-[1,2]benzeno}-7,8-dibromo-5,10-dihydroanthracene-1,4-diyl-(2-methylpropanoate) (1.3 g, 2.3 mmol) in DMF (20 mL) was added CuCN (0.82 g, 10 mmol) was added in one portion. The solution was refluxed, and the reaction was followed by TLC. Then, the solution was cooled down after 6 h when the reaction was done. The reaction mixture was poured into 200 mL of aqueous ammonia and stirred overnight with air bubbling into the solution. The precipitate was filtered and column chromatographed with $CHCl_3$ to yield a pale green solid (0.89 g, 82%). 1H NMR ($CDCl_3$ δ = 7.26) 7.73 (s, 2 H), 7.39–7.41 (dd, J = 5.4, 3.2 Hz, 2H), 7.09–7.12 (dd, J = 5.4, 3.2 Hz, 2 H), 6.83 (s, 2H), 5.50 (s, 2H), 2.97–3.04 (m, 2H), 1.47–1.51 (m, 12H); ^{13}C NMR ($CDCl_3$ δ = 77.0) 175.1, 150.2, 143.4, 141.6, 136.4, 126.5, 128.4, 126.5, 124.6, 120.4, 115.5, 113.2, 48.3, 34.1, 19.2, 19.1; IR (cm^{-1}) ν = 3069, 2977, 2937, 2877, 2234, 1756, 1483, 1467, 1387, 1347, 1322, 1240, 1215, 118, 1123, 1049, 912, 868, 768, 738, 641, 535, 497, 444; $[M^+]$ = 476; UV–vis (CH_2Cl_2) [λ_{max} nm (log ϵ)] 212 (4.52). Anal. Calcd for $C_{30}H_{24}N_2O_4$: C (75.61) H (5.08) N (5.88). Found: C (75.77) H (5.31) N (5.67). Mp 205–206 °C.

{5,10-[1,2]Benzeno}-7,8-dibromo-5,10-dihydro-1,4-dimethoxyanthracene (10). To a stirred solution of 1,4-dimethoxyanthracene (6.82 g, 29 mmol) and 1,2,4,5-tetrabromobenzene (16.9 g, 43 mmol)

in toluene (545 mL) at 0 °C was added *n*-butyllithium (1.6 M in hexane, 27 mL diluted with 200 mL hexane) dropwise. The solution was warmed to room temperature and stirred overnight. The organic layer was dried under vacuum and partitioned between CH_2Cl_2 and water. The organic layer was washed with brine and then dried over anhydrous Na_2SO_4 . The resulting solution was dried under vacuum and column chromatographed with gradient change from hexane/ CH_2Cl_2 (5:1 to 1:1) to yield a white solid (8.3 g, 41%). 1H NMR ($CDCl_3$ δ = 7.26) 7.64 (s, 2 H), 7.38–7.41 (dd, J = 5.3, 3.2 Hz, 2H), 6.99–7.02 (dd, J = 5.3, 3.2 Hz, 2 H), 6.53 (s, 2H), 5.81 (s, 2H), 3.81 (s, 6H); ^{13}C NMR ($CDCl_3$ δ = 77.0) 148.9, 146.8, 144.6, 134.0, 128.7, 125.4, 124.0, 120.3, 109.0, 56.2, 46.4; IR (cm^{-1}) ν = 3069, 2994, 2968, 2939, 2904, 2835, 1606, 1494, 1447, 1362, 1327, 1259, 1073, 796, 787, 767, 734, 711; $[M^+]$ = 472; UV–vis (CH_2Cl_2) [λ_{max} nm (log ϵ)] 206 (4.11), 243 (3.02), 267 (3.50). Anal. Calcd for $C_{22}H_{16}Br_2O_2$: C (55.96) H (3.42). Found: C (56.10) H (3.39). Mp 284–286 °C.

{5,10-[1,2]Benzeno}-1,4-dibenzyloxy-7,8-dibromo-5,10-dihydroanthracene (11). To a stirred solution of 1,4-bis-benzyloxyanthracene (9.5 g, 24 mmol) and 1,2,4,5-tetrabromobenzene (15 g, 39 mmol) in toluene (760 mL) at 0 °C was added *n*-butyllithium (1.6 M in hexane, 27 mL diluted with 100 mL hexane) dropwise. The solution was warmed to room temperature and stirred overnight. The organic layer was dried under vacuum and was partitioned between CH_2Cl_2 and water. The organic layer was washed with brine and then dried over anhydrous Na_2SO_4 . The resulting solution was dried under vacuum and column chromatographed with hexane/ CH_2Cl_2 with gradient change from 5:1 to 1:1 to yield a white solid. (6.3 g, 54%). 1H NMR ($CDCl_3$ δ = 7.26) 7.91 (s, 2 H), 7.83 (s, 2 H), 7.77–7.80 (dd, J = 6.3, 3.3 Hz, 2H), 7.67–7.69 (m, 4 H), 7.40–7.55 (m, 8 H), 7.17 (s, 2H), 5.28–5.38 (m, 4H); ^{13}C NMR ($CDCl_3$ δ = 77.0) 145.1, 140.3, 138.6, 136.3, 131.2, 128.8, 127.9, 127.8, 126.5, 126.3, 125.3, 121.3, 118.8, 85.2, 69.0; IR (cm^{-1}) ν = 3059, 3033, 2919, 1868, 1607, 1497, 1454, 1421, 1386, 1353, 1236, 1193, 1106, 1049, 889, 748, 734, 694, 618, 569, 480. Anal. Calcd for $C_{34}H_{24}Br_2O_2$: C (65.41) H (3.87). Found: C (65.54) H (3.99).

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