Synthesis and Excited-State Photodynamics of A Perylene-Monoimide-Oxochlorin Dyad. A Light-Harvesting Array

Kannan Muthukumaran,[†] Robert S. Loewe,[†] Christine Kirmaier,[‡] Eve Hindin,[‡] Jennifer K. Schwartz,[‡] Igor V. Sazanovich,[‡] James R. Diers,[§] David F. Bocian,^{*,§} Dewey Holten,^{*,‡} and Jonathan S. Lindsey^{*,†}

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, Department of Chemistry, Washington University, St. Louis, Missouri 63130-4899, and Department of Chemistry, University of California, Riverside, California 92521-0403

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A perylene-oxochlorin dyad has been prepared and characterized for potential use as a new light-harvesting motif. The dyad (PMI–ZnO) consists of a perylene-monoimide dye (PMI) joined at the 5-position of a zinc oxochlorin (ZnO) via a diphenylethyne linker. The dyad and its subunits have been studied in both polar and nonpolar media using static and time-resolved optical spectroscopy and electrochemical techniques. Energy flows very rapidly from both unrelaxed (vibrationally, conformationally, or electronically) and relaxed forms of the excited perylene (PMI*) to the ground-state oxochlorin with an effective time constant of ~4 ps and an efficiency of 99% in both toluene and benzonitrile. Subsequently, there is little or no quenching of the excited oxochlorin (ZnO*) in either solvent. These findings are consistent with the expectation that all charge-separated states such as PMI⁻ ZnO⁺ lie energetically above both PMI* and ZnO* in both polar and nonpolar media. Furthermore, light absorption by the perylene and oxochlorin occurs in complementary regions, giving broad spectral coverage. Thus, the new perylene-oxochlorin dyad is an excellent light-harvesting unit that can be incorporated into more elaborate architectures for use in solar-energy and molecular-photonics applications.

Introduction

As part of a program in molecular photonics, we have been working to prepare synthetic architectures that perform functions such as light harvesting and optoelectronic gating.¹ Light harvesting requires efficient energy transfer while optoelectronic gating requires efficient hole/electron transfer. Although porphyrins have provided the foundation for almost all of our work to date, we have recently begun employing pervlene $dyes^{2,3}$ in conjunction with porphyrins to achieve the desired functions.^{4–12} The two types of perylene dyes of interest include perylenebis(imide) dyes and perylene-monoimide dyes, exemplified by PDI-1 and PMI-1, respectively (Chart 1). A principal difference between these two classes is that when joined to porphyrins the pervlene-bis(imide) dyes generally undergo excited-state charge-transfer reactions more readily than their perylenemonoimide counterparts owing to a significant difference in reduction potentials. We have exploited this difference in pervlene reduction potential, differences in oxidation potential of zinc, magnesium, and free-base porphyrins (ZnP, MgP, and FbP), and the different structures of the linker motif (involving aryl and ethyne groups) to tune the absolute and relative yields of energy- and hole/electron-transfer processes in pervleneporphyrin dyads.

For example, dyads comprised of a perylene-monoimide dye and a porphyrin (PMI-ZnP, PMI-ep-ZnP, PMI-ep-FbP, and

CHART 1





PMI-ep-MgP; Chart 2)^{7,13} can be employed as very efficient light-harvesting motifs: the perylene moiety absorbs strongly in the trough between the Soret band and the Q-band of the porphyrin, thereby complementing the weak absorption of light in nonpolar media, perylene-to-porphyrin excited-state energy transfer occurs rapidly and almost quantitatively; there is no subsequent quenching of the excited porphyrin, making the harvested energy available for further utilization. Through proper choice of the porphyrin and linker (e.g., PMI–ZnP), this light-harvesting behavior is essentially retained even in polar media as required by some applications.

On the other hand, dyads comprised of a perylene-bis(imide) and a porphyrin undergo facile hole/electron-transfer reaction

^{*} To whom correspondence should be addressed. (Jonathan S. Lindsey) E-mail: jlindsey@ncsu.edu. (Dewey Holten) E-mail: holten@ wuchem.wustl.edu. (David F. Bocian) E-mail: David.Bocian@ucr.edu.

[†] Department of Chemistry, North Carolina State University.

[‡] Department of Chemistry, Washington University.

[§] Department of Chemistry, University of California.

CHART 2



initiated in either the excited perylene or the excited porphyrin (PDI–ZnP, PDI–FbP, and PDI–MgP; Chart 2).^{5,6} The rates and yields of the processes can be tuned by choice of oxidation potential of the porphyrins. The excited-state electron-transfer properties of these dyads suggest application as efficient charge-separation units for molecular-switching or hole/electron-injection applications.

In a separate line of inquiry, we have developed rational synthetic routes to chlorins^{14–16} and oxochlorins.¹⁷ The synthetic routes provide chlorins or oxochlorins bearing substituents at designated sites at the perimeter of the hydroporphyrin macrocycle. Chlorins and oxochlorins differ from porphyrins in having more strongly allowed absorption in the red in addition to the strong absorption in the blue (Soret band). The important photochemical properties of chlorins and oxochlorins have motivated the development of a number of new syntheses of these green pigments in the past few years.¹⁸

Chlorin/oxochlorin dyads are of particular interest as benchmarks for assessing the extent of electronic communication (i.e., energy transfer and/or electron transfer) involving the corresponding chlorin/oxochlorin monomers. A number of arrays containing chlorin/oxochlorins with various linkages and sites of attachment have been prepared, including the following: (1) chlorins/oxochlorins with electron acceptors such as quinones^{19–25} or C₆₀,^{26–29} (2) chlorins with carotenoid accessory pigments,^{30–32} (3) chlorin/oxochlorins plus porphyrins and pyromellitimides exhibiting energy and charge transfer.^{36,37} We have focused on the oxochlorins owing to their greater stability compared with that of chlorins.

In this paper, we combine these two areas of research to prepare perylene-oxochlorin dyads as shown in Chart 3. One type of dyad incorporates a perylene-monoimide and a zinc oxochlorin (PMI–ZnO) for use in light-harvesting, and is the



subject of the present paper. The other type incorporates a perylene-bis(imide) with a variation in the oxochlorin (PDI-ZnO, PDI-MgO, and PDI-FbO) for applications requiring charge-transfer processes; this set of arrays is examined in the accompanying paper.³⁸ In both cases, the perylene dye provides strong absorption in the green region, complementing the two major absorption bands of the oxochlorin. The attachment of the PMI unit at the meta-position of the oxochlorin meso-phenyl ring provides an architecture of the type that we have used previously with porphyrins in large light-harvesting arrays to suppress cofacial aggregation of the porphyrin macrocycles and thereby achieve enhanced solubility.^{10–12} The dyads have been characterized by electrochemistry, static absorption and fluorescence spectroscopy, and time-resolved fluorescence and transient absorption spectroscopy. Taken together, the studies described herein provide fundamental insight into the design and function of dyad architectures for specific applications in molecular photonics.

Results and Discussion

Synthesis. The synthesis of oxochlorin building blocks relies on the acid-catalyzed condensation of a tetrahydrodipyrrin (Western half) and a 1-bromodipyrromethane-monocarbinol (Eastern half). The resulting tetrahydrobilene-*a* intermediate is subjected to metal-mediated oxidative cyclization forming the chlorin.¹⁴ A regiospecific oxidation then is used to convert the chlorin to the oxochlorin.

The synthesis of the Eastern half begins with a dipyrromethane, which is monoacylated upon reaction with an *S*-2-pyridyl thioate derivative.³⁹ The reaction of 3-bromobenzoyl chloride and 2-mercaptopyridine afforded the acylating agent 1 in 51% yield. Treatment of 5-mesityldipyrromethane (2)⁴⁰ with ethylmagnesium bromide followed by 1 at -78 °C afforded the desired monoacylated dipyrromethane 3 (Scheme 1). Bro-

SCHEME 1



mination of monoacyldipyrromethane **3** with *N*-bromosuccinimide afforded the Eastern-half precursor **4**. This compound was treated with NaBH₄ to afford the monocarbinol (Eastern half). The monocarbinol was reacted with tetrahydrodipyrrin **5** (Western half)¹⁴ under the standard conditions for chlorin formation. The first step entails acid-catalyzed condensation at 0.1 M to afford the tetrahydrobilene-*a* intermediate. The reaction mixture is then diluted 10-fold and treated with the reagents







for metal-mediated oxidative cyclization, employing zinc acetate, silver triflate (AgOTf), and 2,2,6,6-tetramethylpiperidine (TMPi) in refluxing acetonitrile exposed to air. In this manner, the desired zinc chlorin Zn6 was obtained in 37% yield.

We recently developed a simple procedure for oxidation of the methylene group in the reduced ring of the chlorin, forming the corresponding oxochlorin.¹⁷ Thus, treatment of Zn6 with basic alumina (activity I) in toluene at 50 °C in the presence of air gave a mixture of the zinc hydroxychlorin and a trace amount of the zinc oxochlorin. The mixture was then treated with 2,3dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene for 5 min to give the desired zinc oxochlorin ZnO6 in 49% overall yield (Scheme 2).

The perylene-Zn-oxochlorin dyad was synthesized by the Pdcatalyzed coupling of an ethynyl-substituted perylene and a bromo-substituted zinc oxochlorin. The coupling reaction was carried out under similar conditions developed for joining





similarly substituted porphyrins.⁴¹ The conditions employ dilute solutions of the reactants in the presence of tris[dibenzylideneacetone]dipalladium(0) [Pd₂(dba)₃] and tri-*o*-tolylphosphine [P(*o*-tol)₃] in a solution of toluene/triethylamine (TEA) at 60 °C. Thus, the Pd-mediated coupling reaction of bromosubstituted ZnO6 and *N*-(2,6-diisopropyl-4-ethynylphenyl)-9-(4-*tert*-butylphenyloxy)-3,4-perylenedicarboximide (PMI-2)¹⁰ afforded the corresponding dyad PMI–ZnO in 54% yield (Scheme 2). This dyad was purified by column chromatography (silica), preparative size exclusion chromatography (SEC), and column chromatography (silica). The dyad PMI–ZnO was characterized by mass spectrometry, ¹H NMR spectroscopy, and absorption spectroscopy. As reference compounds, we prepared three zinc oxochlorin monomers, ZnO7,³⁸ ZnO8,¹⁷ and ZnO9¹⁷ (Chart 4).

Electrochemical Characterization. The electrochemical data for the dyad PMI–ZnO and benchmark perylene dye PMI-1 are summarized in Table 1. The $E_{1/2}$ values were obtained with square wave voltammetry (frequency 10 Hz). The isolated perylene dye exhibits one oxidation and two reduction waves in the +1.4 to -2.0 V range. The $E_{1/2}$ values for the perylene unit in the dyad are generally similar to those of the isolated dye. The oxochlorin unit in the dyad exhibits two oxidation and two reduction waves in the +1.4 to -2.0 V range; the $E_{1/2}$ values are similar to those of the isolated macrocycle (ref 17 and J. R. Diers and D. F. Bocian, unpublished results). The similarity of the redox potentials of the constituents of the dyad with those of the isolated monomers is indicative of the

	0.	oxidation potentials			reduction potentials			
		oxocl	hlorin	pery	perylene		oxochlorin	
compound	perylene	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(1)$	$E_{1/2}(2)$	
PMI–ZnO PMI-1	$^{+1.05}_{+1.07^{b}}$	+0.54	+0.77	-1.18 -1.21	-1.75 -1.78	-1.57	-1.92	
ZnO9		$+0.59^{\circ}$	+0.89			-1.50	n.m. ^d	

TABLE 1: Half-Wave Potentials $(E_{1/2})^a$

^{*a*} Obtained in butyronitrile containing 0.1 M (*n*-Bu)₄NPF₆. $E_{1/2}$ vs Ag/Ag⁺; $E_{1/2}$ of FeCp₂/FeCp₂⁺ = 0.19 V. The $E_{1/2}$ values are obtained from square wave voltammetry (frequency = 10 Hz). Values are \pm 0.01 V. ^{*b*} This value is for an analogue that lacks the aryloxy group at the perylene 9-position.^{13 c} The same value was reported in ref 17. ^{*d*} Not measured.



Figure 1. Summary diagram showing the excited-state processes in dyad PMI–ZnO at room temperature. The values in parentheses are the estimated free energies of the states in eV (see text).

relatively weak ground-state electronic interactions between the dyad components.

Photophysical Properties. Complete photophysical characterization of dyad PMI–ZnO and reference monomers PMI-1 and ZnO7, ZnO8, ZnO9 was carried out in both toluene and benzonitrile at room temperature. Studies were performed in these two solvents because potential applications may utilize the arrays in either polar or nonpolar media. The photophysical properties of both the dyad and monomers differ only modestly in the two solvents. To aid in the presentation and discussion of the results, Figure 1 summarizes the understanding obtained in this study of the light-driven processes of the perylene-oxochlorin dyad PMI–ZnO.

Absorption Spectra. The ground-electronic-state absorption spectrum of PMI–ZnO is essentially given by the sum of the spectra of the subunits (Figure 2, solid). This finding reflects the relatively weak ground- and excited-state electronic interactions between the perylene and oxochlorin, complementing the conclusion drawn from the electrochemical measurements. The absorption spectrum of PMI–ZnO is dominated by the oxochlorin near-UV Soret band ($S_0 \rightarrow S_3$) at ~424 nm, the oxochlorin $Q_y(0,0)$ band ($S_0 \rightarrow S_1$) at ~610 nm, and the perylene absorption



Figure 2. Absorption spectra (solid) and fluorescence spectra (dashed, dotted) in toluene at room temperature. Emission for the dyad was obtained using primarily excitation of the porphyrin at 392 nm (dashed) or perylene at 480 nm (dotted). The emission intensities in parts A and B have been corrected for the absorbance at the excitation wavelength and on the same scale so that they can be compared. The intensities in C have been reduced by an order of magnitude for clarity of presentation.

contour $(S_0 \rightarrow S_1)$ between 450 and 550 nm. The weak oxochlorin $Q_y(1,0)$ band and Q_x features $(S_0 \rightarrow S_2)$ observed in the spectrum of the isolated chromophore (Figure 2B) underlie the broad perylene absorption contour in the dyad. The latter consists of several unresolved features with an apparent origin at ~540 nm in both the dyad and reference monomer (Figure 2A,C), as is typical for phenoxy-substituted perylene-monoimide dyes.⁷ Similar spectra are observed in benzonitrile, except for a bathochromic shift of ~6 nm in the oxochlorin bands and ~10 nm in the perylene contour (see Supporting Information). For the dyad in either solvent, the blue-green absorption of the perylene accessory pigment complements the blue and red absorption of the oxochlorin, thereby giving broad spectral coverage.

Fluorescence Spectra and Quantum Yields. Fluorescence emission spectra for PMI–ZnO and its reference monomers in toluene at room temperature are shown in Figure 2 (dashed and dotted spectra). The fluorescence spectra in benzonitrile are given in the Supporting Information. For the dyad in either solvent, an emission spectrum was recorded using primarily oxochlorin excitation at 392 nm and primarily perylene excitation at 480 nm. The 392 and 480 nm excitation wavelengths

 TABLE 2: Photophysical Data for Perylene-Oxochlorin

 Dyads and Reference Compounds^a

compound	solvent	PMI* decay $\tau (ps)^b$	$ZnO* \ \phi_{f^c}$	decay τ (ns) ^d
PMI-ZnO	toluene	3.6	0.041	0.8 ± 0.2
	benzonitrile	4.5	0.047	0.6 ± 0.3
ZnO7	toluene		0.037	0.7 ± 0.2
	benzonitrile		0.030	0.7 ± 0.2
ZnO8	toluene		0.040	0.7 ± 0.2
	benzonitrile		0.031	0.6 ± 0.2
ZnO9	toluene		0.044	0.9 ± 0.2
	benzonitrile		0.039	0.9 ± 0.2
PMI-1	toluene	4800 ^e		
	benzonitrile	4500 ^f		

^{*a*} All data at room temperature. ^{*b*} Lifetime of the perylene lowest excited singlet state; the values for the dyads were determined by transient absorption spectroscopy (average single-exponential fit through the PMI bleaching region) and those in the monomers by fluorescence decay (± 200 ps). ^{*c*} Oxochlorin fluorescence yield ($\pm 15\%$) determined using Soret (392 nm) excitation. ^{*d*} Oxochlorin excited singlet state lifetime determined by averaging the values from transient absorption kinetic profiles and fluorescence decay. ^{*e*} From ref 11; the fluorescence yield is 0.82. ^{*f*} The fluorescence yield is 0.71.

were also employed for the oxochlorin and perylene monomers, respectively, and for the free base *meso*-tetraphenylporphyrin (FbTPP) reference compound ($\Phi_F = 0.11$)⁴² used for the fluorescence yield determinations. These excitation wavelengths were chosen to provide a good match in absorption (typically 0.04–0.08) within and among the compounds, selectivity in excitation of each component, and appropriate level of fluorescence so that comparisons of relative intensities would be as reliable as possible.

The fluorescence spectrum for PMI-ZnO in toluene using oxochlorin excitation is identical in shape to that for the isolated chromophore (Figure 2, dashed spectra). The spectrum contains a (0,0) band at 612 nm and a (0,1) band at 670 nm. In the dyad, there is only trace perylene emission (due to minor excitation of this moiety), which can be seen from the trace PMI (0,0)emission near 570 nm (compare dashed spectra in Figure 2). To obtain the oxochlorin fluorescence yield in the dyad, the perylene monomer emission spectrum was normalized to the dyad spectrum in the PMI (0,0) band at \sim 570 nm, and then subtracted to obtain the perylene-free dyad emission spectrum (only a few percent correction in this case). Integration of the resulting spectrum (590-750 nm) and comparison with the FbTPP fluorescence standard ($\Phi_{\rm f} = 0.11$)⁴² gives an oxochlorin fluorescence yield of $\Phi_f = 0.041$ for PMI–ZnO in toluene. This value is the same within experimental error as $\Phi_{\rm f} = 0.037$ to 0.044 measured for the monomers ZnO7-ZnO9 (Table 2). This result can be seen from visual inspection of the emission spectra for the dyad and monomer in Figure 2 (dashed spectra), which have been corrected for small differences in the absorbance at the excitation wavelength. Similarly, the fluorescence yield for the dyad in benzonitrile is comparable to or slightly larger than those for the reference compounds (Table 2). The finding of comparable oxochlorin emission for the PMI-ZnO dyad and the reference monomers indicates that the excited oxochlorin (ZnO*) is not quenched appreciably if at all by charge (electron) transfer to the pervlene component of the dyad in either toluene or benzonitrile (see Figure 1).

Excitation of PMI–ZnO in toluene using perylene excitation at 480 nm gives the dotted spectrum in Figure 2A (corrected for absorbance at the excitation wavelength). The perylene emission is larger in this case (compared to using 392 nm excitation), as indicated by the increased PMI (0,0) emission at \sim 570 nm. There are several key aspects of these results. (1)

After subtraction of the perylene emission as outlined above, the intensity of oxochlorin emission in the dyad is comparable to that obtained using primarily oxochlorin excitation (compare dotted and dashed spectra in Figure 2A, using the PMI monomer emission in Figure 2C as a reference). This observation reflects a high yield of perylene-to-oxochlorin excited-state energy transfer. (2) The perylene emission obtained using perylene excitation is about \sim 100-fold less than in the isolated dye. This result also reflects substantial energy transfer from PMI* to the oxochlorin. [Although hole transfer would also quench the perylene emission, this process is insignificant in this case (Figure 1A), as will be described below.] (3) The pervlene emission that is observed derives largely from the high intrinsic fluorescence yield ($\Phi_f \sim 1$) of this chromophore. Thus, residual perylene emission in the dyad is expected to be of the same order as that from the oxochlorin ($\Phi_f \sim 0.04$) even if the perylene emission is quenched in the dyad due to energy (or hole) transfer to the oxochlorin with an efficiency of >95%. A similar situation applies to pervlene-porphyrin dyads that we have studied previously.⁵⁻⁷ (4) Due to high/low intrinsic perylene/ oxochlorin fluorescence, it follows that even trace perylene impurity (e.g., from minor decomposition) can compromise the use of the static emission data to quantitate the yield of peryleneto-oxochlorin energy transfer. Thus, the energy-transfer yields will be derived from the time-resolved absorption measurements described below.

Fluorescence Lifetimes. A second assay of possible oxochlorin charge-transfer quenching in dyad PMI–ZnO is obtained from comparison of the excited-singlet-state lifetime with that for a zinc oxochlorin reference compound in the same solvent. A ZnO* lifetime of 0.8 ± 0.2 ns was measured for PMI–ZnO in toluene and 0.7 ± 0.2 ns in benzonitrile using fluorescence detection. The excited-state lifetimes (± 0.2 ns) for reference monomers ZnO7, ZnO8, and ZnO9 in toluene are 0.8, 0.6, and 0.9 ns, respectively, while the values in benzonitrile are 0.9, 0.7, and 0.9 ns. The lifetimes measured by transient absorption were comparable to or somewhat shorter than those determined by fluorescence. Average values from the two methods are given in Table 2. Some of the fluorescence measurements on the dyad indicated the presence of a second component that may represent a trace amount of (free) perylene emission ($\tau = 3-5$ ns).

Time-Resolved Absorption Spectra. Figure 3 shows timeresolved absorption difference spectra for PMI-ZnO in toluene (part A) and benzonitrile (part B) at selected pump-probe time delays. The results are generally similar in the two solvents, so the two cases will be presented together. In each solvent, the initial spectrum (0.5 ps; solid) was constructed from a series of spectra acquired at very closely spaced time intervals to account for the time dispersion of wavelengths in the white-light probe pulse. This initial spectrum can be associated primarily with the excited perylene (PMI*) produced by direct perylene excitation (483 or 495 nm). The broad trough from 500 to 570 nm reflects bleaching of the pervlene ground-state absorption contour (see solid spectrum in Figure 2C) and stimulated (by the white-light probe pulse) emission from PMI* that occurs in the same region as the spontaneous fluorescence (see dashed spectrum in Figure 2C). The expected vibronic-overtone stimulated-emission features underlie the opposing, pronounced PMI* transient absorption that has a maximum between 600 and 620 nm and extends to \sim 700 nm. The small dip at \sim 610 nm on the top of the PMI* transient absorption of PMI-ZnO in either toluene or benzonitrile (Figure 3A) can be attributed to a combination of (1) oxochlorin ground-state $Q_{\nu}(0,0)$ bleaching due to perylene-oxochlorin electronic coupling in the dyad that



Figure 3. Transient absorption spectra at selected pump-probe delay times for dyad PMI-ZnO in (A) toluene and (B) benzonitrile following excitation with a 130 fs flash at (A) 495 nm or (B) 483 nm.

leads to effects on the oxochlorin when PMI* forms, (2) oxochlorin bleaching or excited-state stimulated-emission caused by direct minor excitation of the oxochlorin, or (3) bleaching and stimulated emission due to the initial stage of rapid energy transfer from PMI* to the oxochlorin.

By ~30 ps for PMI–ZnO in either toluene or benzonitrile, the PMI ground-state bleaching and PMI* stimulated-emission features have basically disappeared and have been replaced by features that can be associated primarily with the lowest excited singlet state (ZnO*) of the zinc oxochlorin (Figure 3, dashed spectra). The feature at ~610 nm in the 30 ps spectra contains comparable contributions of $Q_y(0,0)$ ground-state bleaching and ZnO* stimulated emission, the small dip at ~670 nm is $Q_y(0,1)$ stimulated emission, and the small dip at ~570 nm is $Q_y(1,0)$ bleaching; all of these contributions are in keeping with the positions and relative amplitudes of the features of the static absorption and fluorescence spectra (Figure 2B). The excited state ZnO* also has a relatively weak and featureless transient absorption across the entire region displayed.¹⁷

The ZnO* stimulated-emission contributions at ~30 ps decay substantially as time proceeds so that by ~3.4 ns the major feature is oxochlorin $Q_y(0,0)$ ground-state bleaching at ~610 nm, along with $Q_y(1,0)$ bleaching at ~570 nm and a relatively weak, featureless transient absorption across the spectrum (Figure 3, dotted spectra). The 3.4 ns spectrum for PMI–ZnO in either toluene or benzonitrile can be assigned primarily to the oxochlorin lowest excited triplet state (ZnO^T). The fact that the ZnO^T $Q_y(0,0)$ bleaching is roughly one-half the magnitude of the combined ZnO* $Q_y(0,0)$ bleaching plus stimulatedemission indicates that the yield of ZnO* \rightarrow ZnO^T intersystem crossing (the triplet yield) is very high, as we have found for zinc oxochlorin monomers (see Figure 5C).¹⁷

In summary, the transient absorption difference spectra are consistent with the PMI* $ZnO \rightarrow PMI ZnO^*$ energy transfer followed by PMI $ZnO^* \rightarrow PMI ZnO^T$ intersystem crossing (plus some internal conversion and fluorescence) being the primary excited-state processes that occur following photoexcitation of PMI–ZnO in either toluene or benzonitrile (Figure 1). Along



Figure 4. Kinetic traces and multiexponential fits at selected wavelengths for PMI–ZnO from the same measurements depicted in Figure 3B.

these lines, the apparent lack of PMI bleaching (500-550 nm) following PMI* decay in toluene (Figure 3A, dashed spectrum) indicates that $PMI^* ZnO \rightarrow PMI^- ZnO^+$ hole transfer has not occurred to a measurable degree, as the charge-separated state would give PMI bleaching. This finding indicates that the charge-separated state must lie above PMI* in free energy for PMI-ZnO in toluene, as is indicated in Figure 1A. [The redox potentials indicate that PMI⁺ ZnO⁻ must lie substantially higher in energy than PMI⁻ ZnO⁺.] Similarly, there is possibly only a very small PMI bleaching at 30 ps in benzonitrile (Figure 3B, dashed), indicating that PMI* $ZnO \rightarrow PMI^- ZnO^+$ hole transfer has a yield of at most \sim 20% in this case. Thus, even with solvent stabilization in the polar medium, state PMI⁻ ZnO⁺ lies above or close to PMI* in free energy, as is shown in Figure 1B. Similarly, as ZnO* subsequently decays (and ZnO^T forms), there is no indication that PMI bleaching develops in either solvent (Figure 3A and 3B, dotted). The latter result indicates that PMI $ZnO^* \rightarrow PMI^- ZnO^+$ electron transfer is insignificant, consistent with the charge-separated state lying well above ZnO* in both solvents (Figure 1). These conclusions are supported by additional analysis given below.

Although the above description of the key features in the transient absorption spectra presents a straightforward analysis of the excited-state behavior of PMI–ZnO in polar and nonpolar media, there is actually quite significant underlying complexity. This behavior is illustrated by the series of kinetic traces for PMI–ZnO in benzonitrile shown in Figure 4. Part A shows decay of PMI bleaching plus stimulated emission at 510 nm, along with a single-exponential fit (on the time scale shown) with $\tau = 5.5$ ps and a marginally better dual-exponential fit with $\tau_1 = 2.0$ ps and $\tau_2 = 7.8$ ps. Panel B shows the growth of oxochlorin bleaching plus stimulated emission at 615 nm and a fit with $\tau = 6.0$ ps, while part D shows that $\tau = 2.1$ ps at 630 nm. The kinetic profile at 565 nm (part C) unequivocally demonstrates the presence of two kinetic components (2.6 and



Figure 5. (A) Species-associated spectra from multiexponential global analysis of the same data set depicted for dyad PMI–ZnO in Figures 3B and 4, using the model described in the text. Transient absorption spectra at selected pump–probe delay times for samples in benzonitrile at room temperature are shown in (B) for perylene monomer PMI-1 (483 nm excitation) and in part C for oxochlorin monomer ZnO8 (540 nm excitation).

11 ps) on this time scale because at this wavelength the components enter with opposite signs (one is a growth and the other a decay), and similar results are found at 645 nm (part E). Global analysis was performed on the kinetic profiles at the above five wavelengths and about 30 others obtained across the entire spectral region shown in Figure 3 (500-730 nm), spanning times before and during the excitation flash and extending to ~ 3.5 ns (using a function containing three exponentials and "constant" long-time asymptote ($\tau > 3$ ns) plus the instrument response). On the short time scale (<50 ps) shown in Figure 4, the best-fit time constants are $\tau_1 = 2$ ps and $\tau_2 = 8$ ps; on the longer time scale (25 ps to 3.5 ns) a third component has $\tau_3 \sim 400$ ps (see inset to Figure 4B). Although there are clearly three kinetic components, and two contributing at times <50 ps, the simple scheme described above (Figure 1) indicates there should be only two states that decay on the time scale of the measurements, namely, PMI* and ZnO*.

The origin of the three kinetic components is demonstrated in Figure 5, which shows species-associated spectra derived from the global analysis of the data set for the PMI-ZnO in benzonitrile (part A) along with key spectra for the reference monomers PMI-1 (part B) and ZnO8 (part C) in the same solvent. (Spectra similar to those for ZnO8 were found for ZnO7.) A central aspect of this analysis derives from the finding that the PMI-1 monomer exhibits two distinct spectra at early times (<50 ps) after excitation (Figure 5B) even though the lowest excited singlet state (PMI*) does not decay over the course of the transient absorption measurements because this state has a lifetime of \sim 5 ns (as deduced by fluorescence decay; Table 2). As we will report elsewhere, ¹³ both monomer transient difference spectra can be assigned to PMI* but differ in shape due to a shift of the stimulated-emission contribution with time (analogous to a dynamic Stokes shift) plus possible additional changes in the transient absorption contribution. The time constant of this PMI* relaxation is \sim 3 ps for PMI-1 in benzonitrile. The nature of the relaxation (conformational, vibrational, and electronic) for a series of perylene dyes is under investigation via experiment and theory and will be reported on in detail elsewhere.¹³

The finding of such complexity in the photophysics of even the simple, isolated perylene dye prompted the use of a kinetic model in the global analysis for dyad PMI-ZnO in benzonitrile (Figures 3 and 4) in which there are two forms of PMI*, one unrelaxed and the other relaxed, both of which can undergo energy transfer to make ZnO*, which in turn decays to make ZnO^T (and the ground state). [The amplitude (preexponential factor) spectra from the global analysis assuming three simple independent exponentially decaying components is given in the Supporting Information.] The resulting species-associated spectrum of the 2 ps component (Figure 5A, black) and 8 ps component (red) match the respective experimental spectra at 0.5 and 40 ps for the PMI-1 monomer (Figure 5B) in terms of shape and the peak wavelengths of the major features. Thus, the early-time behavior for the dyad involves both a relaxation (conformational/vibrational/electronic) within PMI* as well as the population decay of this electronic state. It is significant that the peak at \sim 570 nm in the 40 ps spectrum for the perylene monomer (Figure 5B, red) is slightly larger than in the peak at \sim 600 nm in the 0.5 ps spectrum (black), whereas the reverse is true in the corresponding species-associated spectra for the dyad (Figure 5A). This difference can be ascribed to energy transfer from PMI* to the oxochlorin in the dyad already occurring to some degree during the 2 ps kinetic phase (in competition with relaxation within PMI*), with the remainder occurring during the 8 ps kinetic phase (primarily electronic decay of the relaxed excited state). Thus, energy transfer during the 2 ps phase siphons off part of the PMI* population, so that spectrum of the relaxed form of the state in the dyad has a smaller magnitude (relative to the unrelaxed form) compared to the situation in the isolated dye. Thus, in assessing the rate of energy transfer for PMI-ZnO in benzonitrile, we will use an average time constant of \sim 4.5 ps obtained from single-exponential fits across the PMI bleaching (500-530 nm), which provides a measure of the return of PMI* (relaxed plus unrelaxed forms) to the ground state as electronic energy shifts to the oxochlorin to produce ZnO*. [Assessing the early time dynamics is further complicated because ZnO* may also have a relaxation process that occurs on the time scale of 10-15 ps, as judged from studies on an isolated oxochlorin.¹⁷]

The species-associated spectrum of the 400 ps component for the dyad (Figure 5A, green) and the subsequent spectrum (blue) that does not decay on the time scale of the transient absorption experiment ($\tau > 3$ ns) are readily interpreted. These calculated spectra are basically the same as the experimental spectra observed at early and long times for the ZnO8 monomer (part C) and other reference monomers (not shown), and at 40 ps and 3.4 ns for the dyad (Figure 3B, dashed and dotted) that were described above. Thus, the species-associated spectra for the third and "constant" kinetic components for the dyad can be assigned to the oxochlorin excited states ZnO* and ZnO^T. The average ZnO* lifetime from the transient absorption and fluorescence experiments for PMI–ZnO in benzonitrile is 0.6 ns (Table 2).

Similar complexity in the early-time dynamics is found for PMI–ZnO in toluene, although the spectral changes during the PMI* relaxation phase are less pronounced than in benzonitrile. These differences are in accord with the PMI* relaxation effects

found for the PMI-1 monomer in toluene versus benzonitrile.13 An effective PMI* lifetime of \sim 3.6 ps is obtained from the single-exponential fits across the PMI bleaching (Table 2), which primarily reflects energy transfer to the oxochlorin (from both the unrelaxed and relaxed forms of the excited perylene). It should be noted that without correlation of comprehensive data for the dyad and monomer, the finding of more pronounced spectral evolution for the dyad in polar medium could have been taken to imply greater participation of a charge-separated state such as PMI⁻ ZnO⁺. Such a possibility would have been further attractive because the electrochemically generated PMI-1 anion has a pronounced band at ~ 600 nm;¹³ however, the excitedstate feature at approximately the same position has comparable intensity (see Figure 3B, solid, and 5B). These combined data make it difficult to use such absorption features alone as a diagnostic for the formation of a charge-separated state.

Energies of the Electronic States of the Dyads. In constructing the state diagram shown in Figure 1, the energies of the excited perylene and porphyrin components were taken directly from the spectroscopic data for the dyad. In particular, the average energies of the (0,0) absorption and fluorescence bands of the two components of each array were used to obtain the energies of the lowest excited singlet state in both solvents. The free energy of the charge-separated state PMI⁻ ZnO⁺ was derived using an experimentally determined⁶ reference value of 2.05 eV for state PDI⁻ ZnP⁺ in the perylene-porphyrin dyad PDI-ZnP in toluene, which differs from dyad PMI-ZnO studied here in both the perylene and tetrapyrrole components but has a similar linker. In particular, the state PMI⁻ ZnO⁺ in PMI-ZnO is higher than the state PDI⁻ ZnP⁺ in PDI-ZnP by a total of 0.48 eV from two sources: (1) the \sim 80 mV more positive oxidation potential of zinc oxochlorins versus zinc porphyrins (Table 1)^{6,17} and (2) the 0.4 eV more negative reduction potential of the perylene-monoimide versus perylenebis(imide) dye (Table 1).⁵ Finally, the charge-separated state will be stabilized by 0.26 eV in benzonitrile versus toluene (estimated using the simple Coulomb interaction $e^{2/(\epsilon_s r)}$, where $e^2 = 14.45 \text{ eV} \cdot \text{Å}$, r is the oxochlorin-perylene center-to-center separation (~21 Å), and ϵ_s is the static dielectric constant (2.38 for toluene and 25.2 for benzonitrile)).

Rates and Yields of the Energy- and Charge-Transfer Processes. The transient absorption data described above indicate that the excited perylene (PMI*) in the dyad decays primarily by energy transfer to the oxochlorin, with hole transfer being minimal (Figure 1). Energy transfer causes PMI* to have a lifetime that is about 3 orders of magnitude shorter than the lifetime of ~ 5 ns in the isolated dye, with an average value (unrelaxed and relaxed forms) of 3.5-5 ps (Table 2). The rate constant and quantum yield of PMI* ZnO → PMI ZnO* energy transfer in toluene are obtained by applying standard methods⁵ to the PMI* lifetimes for the PMI-ZnO dyad and ZnO7 reference monomer in Table 2. The results are $k_{\rm ENT}$ = $[(3.6 \text{ ps})^{-1} - (4800 \text{ ps})^{-1}]^{-1} \sim (3.6 \text{ ps})^{-1}$ and $\Phi_{\text{ENT}} =$ [1 - 3.6/4800]·100 >99%. The energy-transfer yield for PMI-ZnO is >99% in benzonitrile as well. It is interesting to note that even though PMI-ZnO energy transfer is very rapid and basically quantitative, it is about 40% slower than we observed previously for dyad PDI-ZnP (Chart 2) that contains a perylenebis(imide) dye and a zinc porphyrin employing the same linker motif.5 This difference is likely due to the predominant throughbond (Dexter) nature of energy transfer in these systems^{1,5} together with a weaker electronic coupling in PMI-ZnO compared to PMI-ZnP. A reduced through-bond coupling in the oxochlorin-containing dyad is anticipated¹ because (1) the

HOMO (the a_{1u}-like orbital) in this macrocycle has much lower electron density at the meso-carbon linker-attachment site than the HOMO (the a_{2u} orbital) in the porphyrin-containing dyad and (2) the meta-phenyl position to which the ethyne group of the linker is attached has less electron density than the paraphenyl position utilized in the porphyrin-containing dyad.⁴³ Efficient excited-state energy transfer also has been observed from a porphyrin (or other tetrapyrrole chromophore) to a chlorin/oxochlorin.33-37 Energy transfer from a carotenoid accessory pigment to a chlorin is also quite fast (~ 14 ps) and moderately efficient (\sim 50%) at an inter-chromophore separation of ~ 2 Å using attachment at a β -pyrrole position that is contained in the conjugation path of the macrocycle, but is very slow (>1 ns) and inefficient (<10%) at a distance of \sim 5 Å using attachment at the reduced ring of the hydroporphyrin.^{31,32} Collectively, these studies show that rapid and efficient photoinduced energy transfer to chlorins/oxochlorins can be achieved, and with characteristics that depend on the chromophores and linker motifs employed.

In an ideal light-harvesting array, the harvested energy transferred to the acceptor chromophore should not be wasted by charge-transfer processes involving the accessory pigment. The transient absorption spectra for PMI-ZnO in toluene or benzonitrile show no evidence for electron transfer to the perylene, implying that ZnO* decays primarily by the normal routes open to the isolated chromophore (mainly intersystem crossing to the excited triplet state). The same conclusion is reached upon comparison of the lifetime and fluorescence yield of the excited oxochlorin in the dyad compared to the values in the reference monomers using standard equations.⁵ The ZnO* fluorescence quantum yields in the dyad are comparable to or slightly larger than in the reference monomers in both solvents, and similarly the average (fluorescence and transient absorption) ZnO* lifetime in the dyad and monomer in toluene (0.8 ± 0.2) ns) is the same within experimental error, both results indicating no excited-state quenching. In benzonitrile the slightly shorter average lifetime of 0.6 ± 0.2 ns in the dyad versus 0.7 ± 0.2 ns in the monomers suggests that there may be some electrontransfer quenching of ZnO* with a yield $\Phi_{\text{ET}} = [1 - 0.6/0.7]$. $100 \sim 15\%$ in this polar medium. However, the yield could be zero within experimental uncertainty by this calculation, in agreement with the other measurements. Additionally, the analysis given above, showing no evidence for PMI* hole transfer and with PMI⁻ ZnO⁺ lying energetically above PMI^{*}, would also place the charge-separated state well above ZnO*, making quenching of the latter state unlikely. Taken as a whole, the results indicate that PMI $ZnO^* \rightarrow PMI^- ZnO^+$ electron transfer is not significant for PMI-ZnO in either toluene or benzonitrile (Figure 1). Thus, ZnO* has decay characteristics comparable to those of the isolated chromophore in both polar and nonpolar media. It follows that the composition of the dyad provides no impediment for use of the electronic energy placed in the excited oxochlorin either by direct excitation or efficient energy transfer from the perylene accessory pigment.

Conclusions and Outlook

We have synthesized and characterized a new peryleneoxochlorin dyad for potential use in light-harvesting applications. This dyad is a first step beyond our previous studies of peryleneporphyrin arrays in combining accessory pigments and hydroporphyrins to elicit desirable photophysical properties. The incorporation of the oxochlorin was intended to simultaneously provide stronger absorption in the red spectral region compared to porphyrins while maintaining similar redox characteristics. The latter factors led to the choice of oxochlorins compared to their close chlorin relatives, the former macrocycle being harder to oxidize and more stable than the latter but with comparable red absorption.

The results demonstrate that the new perylene-oxochlorin dyad (PMI-ZnO) studied here has many favorable qualities as a light-harvesting unit: energy flows rapidly (~ 4 ps) and efficiently (99%) from perylene to oxochlorin, which then shows excited-state decay characteristics comparable to those of the isolated chromophore in both polar and nonpolar media. Thus, incorporation of the perylene-monoimide as an accessory pigment to complement the absorption of the oxochlorin has not resulted in unwanted charge-transfer decay pathways. Such processes would compromise the availability of the harvested energy for subsequent transfer from the excited oxochlorin to another stage in a larger architecture. On the other hand, charge transfer can be elicited through appropriate tuning of energy levels of the perylene and/or oxochlorin, thereby converting a light-harvesting motif into a charge-separation unit for switching or charge-injection applications in molecular optoelectronics. A description of perylene-oxochlorins wherein charge separation is the dominant excited-state process is provided in the companion paper.

Experimental Section

General. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded in CDCl₃. Mass spectra were obtained by high-resolution fast atom bombardment mass spectrometry (FAB-MS) and by laser desorption mass spectrometry (LD-MS) in the absence of a matrix.⁴⁴ Absorption and emission spectra were collected in toluene at room temperature unless noted otherwise. Melting points are uncorrected. Alumina (activity grade I) was obtained from Fisher. Silica gel (Baker, 40 μ m average particle size) was used for column chromatography. Preparative SEC was performed using BioRad Bio-Beads SX-1 (200-400 mesh) beads. Analytical SEC was performed using a 1000 Å column (flow rate = 0.800 mL/min; solvent = tetrahydrofuran (THF); quantitation at 420 and 520 nm; reference at 475 and 590 respectively; oven temperature 40 °C; or quantitation at 520 and 610 nm; reference at 575 and 670, respectively; oven temperature 25 °C).

Solvents. Toluene and triethylamine were freshly distilled from CaH_2 and sparged of oxygen prior to use. THF was distilled from sodium benzophenone ketyl as required. CH_3CN was distilled from CaH_2 and stored over molecular sieves. Anhydrous methanol was prepared by drying over CaH_2 for 12 h followed by distillation. All other solvents were used as received.

Noncommercial Compounds. The syntheses of dipyrromethane **2**,⁴⁰ Western half **5**,¹⁴ and perylene PMI-2¹⁰ have been described previously.

S-2-Pyridyl 3-bromobenzothioate (1). Following a general procedure,³⁹ a solution of 2-mercaptopyridine (11.1 g, 0.100 mol) in CH₂Cl₂ (400 mL) was treated with a solution of 3-bromobenzoyl chloride (13.2 mL, 0.100 mol) in CH₂Cl₂ (100 mL) via a pressure equalizing dropping funnel over 20 min. A solid precipitated when about half of the acid chloride solution was added. Then CH₂Cl₂ (300 mL) and 2N aqueous NaOH solution were added. The organic phase was separated, washed with water, dried (MgSO₄), and concentrated. The solid obtained was crystallized from hexanes to afford a colorless solid (15.1 g, 51%): mp 63–65 °C. ¹H NMR δ: 7.32–7.42 (m, 2H), 7.68–7.76 (m, 2H), 7.77–7.84 (m, 2H), 8.11–8.14 (m, 1H), 8.66–8.72 (m, 1H); ¹³C NMR δ 122.96, 123.80, 126.05, 130.27,

130.33, 130.71, 136.64, 137.23, 138.11, 150.54, 150.62, 188.00. Anal. Calcd for $C_{12}H_8BrNOS$: C, 49.00; H, 2.74; N, 4.76. Found: C, 49.07; H, 2.75; N, 4.78.

1-(3-Bromobenzoyl)-5-mesityldipyrromethane (3). Following a general procedure,³⁹ a solution of EtMgBr in THF (10 mL, 10 mmol, 1.0 M) was added to a solution of 5-mesityldipyrromethane (2, 1.06 g, 4.00 mmol) in dry THF (4 mL) at room temperature. After stirring for 10 min, the flask was cooled to -78 °C and a solution of 1 (1.18 g, 4.00 mmol) in THF (4 mL) was added. The cooling bath was removed and the mixture was stirred for 30 min. The reaction was quenched with saturated aqueous NH₄Cl. The mixture was extracted with CH₂Cl₂. The organic layer was washed with water, dried (Na2SO4) and concentrated to give a dark residue. Column chromatography [silica, $CH_2Cl_2 \rightarrow CH_2Cl_2$ /ethyl acetate (95:5)] afforded a pale brown foamlike solid. Recrystallization from hexanes provided a pale yellow solid (1.21 g, 68%): mp 208 °C (dec). ¹H NMR δ: 2.09 (s, 6H), 2.30 (s, 3H), 5.95 (s, 1H), 6.10-6.16 (m, 2H), 6.20-6.24 (m, 1H), 6.67-6.71 (m, 1H), 6.81-6.84 (m, 1H), 6.90 (s, 2H), 7.32 (t, J = 8.0 Hz, 1H), 7.64–7.69 (m, 1H), 7.74–7.79 (m, 1H), 7.80–7.88 (br, 1H), 7.96 (t, J = 1.6 Hz, 1H), 9.15–9.28 (br, 1H); ¹³C NMR δ 20.75, 20.89, 38.72, 107.34, 109.07, 110.41, 117.04, 120.95, 122.53, 127.44, 128.90, $129.52,\,129.94,\,130.71,\,131.80,\,132.95,\,134.53,\,137.42,\,137.51,$ 140.43, 141.62, 182.32. Anal. Calcd for C₂₅H₂₃BrN₂O: C, 67.12; H, 5.18; N, 6.26. Found: C, 67.00; H, 5.25; N, 6.22.

1-Bromo-9-(3-bromobenzoyl)-5-mesityldipyrromethane (4). Following a general procedure,^{14,15} a solution of **3** (895 mg, 2.00 mmol) in 20 mL of dry THF was cooled to -78 °C under argon. A sample of N-bromosuccinimide (NBS, 356 mg, 2.00 mmol) was added and the reaction mixture was stirred for 1 h at -78 °C. Hexanes (50 mL) and water (50 mL) were added and the mixture was allowed to warm to room temperature. The mixture was extracted with CH₂Cl₂. The organic layer was dried (Na₂SO₄) and concentrated under reduced pressure without heating. Column chromatography [silica, hexanes/ethyl acetate $(9:1) \rightarrow (4:1)$] afforded a pale yellow powder (930 mg, 88%): ¹H NMR δ: 2.10 (s, 6H), 2.30 (s, 3H), 5.88 (s, 1H), 6.00-6.03 (m, 1H), 6.10–6.17 (m, 2H), 6.80–6.83 (m, 1H), 6.91 (s, 2H), 7.34 (t, J = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.70-7.80 (br, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.97 (s, 1H), 9.11-9.21 (br, 1H). This compound was unstable and decomposed while recording a ¹³C NMR spectrum. However, adequate stability over the course of 2 days was achieved upon storage as a solid at 0 °C.

5-(3-Bromophenyl)-17,18-dihydro-10-mesityl-18,18-dimethylporphinatozinc(II) (Zn6). Following a standard procedure,¹⁴ a solution of **4** (526 mg, 1.00 mmol) in THF/methanol [40 mL (4:1)] was treated with NaBH₄ (0.380 mg, 10.0 mmol). After 15 min (TLC indicated complete reaction), the reaction mixture was quenched with cold water and extracted with CH₂Cl₂. The organic layer was dried (K₂CO₃) and concentrated under reduced pressure without heating to afford the monocarbinol. The foamlike residue was dissolved in 10 mL of CH₃CN. Then 5 (190 mg, 1.0 mmol) was added followed by TFA (77 μ L, 1.0 mmol). The reaction mixture was stirred at room temperature for 30 min, and then diluted with 90 mL of CH₃CN. Samples of AgOTf (771 mg, 3.00 mmol), Zn(OAc)₂ (2.75 g, 15.0 mmol), and 2,2,6,6-tetramethylpiperidine (5.10 mL, 30.0 mmol) were added. The resulting mixture was refluxed for 18 h. The reaction mixture was concentrated. The residue thus obtained was chromatographed [silica, hexanes/CH₂Cl₂ (2: 1)] to afford a blue solid (252 mg, 37%): ¹H NMR δ : 1.85 (s, 6H), 2.01-2.04 (m, 6H), 2.59 (s, 3H), 4.52 (s, 2H), 7.21 (s, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.82–7.87 (m, 1H), 8.00–8.03 (m, 1H), 8.20–8.24 (m, 1H), 8.26 (d, J = 4.4 Hz, 1H), 8.31 (d, J = 4.4 Hz, 1H), 8.51 (d, J = 4.4 Hz, 1H), 8.58–8.60 (m, 1H), 8.63 (d, J = 4.4 Hz, 1H), 8.65 (s, 1H), 8.68 (d, J = 4.4 Hz, 2H). LD-MS observed: 674.62. FAB-MS observed: 674.0999. Calcd: 674.1024 (C₃₇H₃₁BrN₄Zn). λ_{abs} 412 and 609 nm.

5-(3-Bromophenyl)-17,18-dihydro-10-mesityl-18,18-dimethyl-17-oxoporphinatozinc(II) (ZnO6). Following a standard procedure,¹⁷ a solution of Zn6 (156 mg, 0.230 mmol) in toluene (12 mL) was treated with basic alumina (activity I, 10 g). The mixture was heated to 50 °C with constant stirring under an air atmosphere. After 66 h, TLC examination showed complete consumption of starting material. The mixture was filtered. The filtered material was washed with CH2Cl2/methanol (19:1) until the washings were colorless. The filtrate was concentrated under reduced pressure to give a bluish-green solid. The latter was dissolved in toluene (115 mL) and treated with DDQ (104 mg, 0.460 mmol). The reaction mixture was stirred at room temperature for 5 min and quenched with triethylamine. The reaction mixture was concentrated under reduced pressure and chromatographed (silica, CH₂Cl₂) to afford a bluish-purple solid (78 mg, 49%): ¹H NMR δ : 1.82 (s, 6H), 2.01 (s, 6H), 2.61 (s, 3H), 7.24 (s, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.80-7.90 (m, 1H), 8.04 (d, J = 7.6 Hz, 1H), 8.24–8.27 (m, 1H), 8.40-8.55 (m, 2H), 8.67 (d, J = 4.4 Hz, 1H), 8.78 (d, J = 4.4 Hz, 1H), 8.92-8.99 (m, 3H), 9.50-9.52 (m, 1H). Anal. LD-MS observed: 688.94. FAB-MS observed: 688.0829. Calcd: 688.0816 (C₃₇H₂₉BrN₄OZn). λ_{abs} 422 and 609 nm.

5-[3-[2-[4-[9-(4-tert-Butylphenyloxy)perylene-3,4-dicarboximido]-3,5-diisopropylphenyl]ethynyl]phenyl]-17,18-dihydro-10-mesityl-18,18-dimethyl-17-oxoporphinatozinc(II) (PMI-ZnO). Following a standard procedure,⁴¹ samples of ZnO6 (35.0 mg, 50.0 µmol), PMI-2 (33.0 mg, 50.0 µmol), Pd₂(dba)₃ (7.3 mg, 8.0 μ mol) and P(o-tol)₃ (19.5 mg, 64.0 μ mol) were placed in a Schlenk flask and pump-filled with argon three times. A solution of toluene/triethylamine [21 mL (5:1)] was then added. The mixture was heated to 60 °C with stirring for 1 h. The reaction mixture was cooled to room temperature and filtered through a pad of Celite. The filtered material was washed with CHCl₃ until the washings were colorless. The filtrate was concentrated under reduced pressure to afford a dark purple solid. Purification was achieved by chromatography (silica, CHCl₃), preparative SEC (THF), and chromatography (short silica column, CHCl₃). The resulting solid was washed with methanol, affording a pale-purple solid (34 mg, 54%) that was homogeneous by analytical SEC: ¹H NMR δ : 1.17 (d, J =6.4 Hz, 12H), 1.37 (s, 9H), 1.84 (s, 6H), 2.06 (s, 6H), 2.61 (s, 3H), 2.70-2.78 (m, 2H), 6.96 (d, J = 8.4 Hz, 1H), 7.08-7.14(m, 2H), 7.25 (s, 2H), 7.42-7.49 (m, 2H), 7.53 (s, 2H), 7.64-7.74 (m, 2H), 7.94-7.98 (m, 1H), 8.06-8.09 (m, 1H), 8.25-8.36 (m, 3H), 8.43-8.46 (m, 2H), 8.49-8.57 (m, 4H), 8.58-8.68 (m, 3H), 8.85 (d, J = 4.8 Hz, 1H), 8.92–9.00 (m, 2H), 9.59 (s, 1H). LD-MS observed: 1264.66. FAB-MS observed: 1261.44. Calcd: 1261.45 (C₈₃H₆₇N₅O₄Zn). λ_{abs} 423, 513, and 610 nm.

Characterization. The electrochemical and spectroscopic studies were conducted using instrumentation and techniques previously described.⁵ Transient absorption measurements used $5-10 \ \mu\text{M}$ samples at room-temperature excited with ~130 fs, $20-30 \ \mu\text{J}$, and 480-600 nm pulses.

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Supporting Information Available: Absorption and emission spectra for PMI–ZnO and its component monomers in benzonitrile, amplitude-associated spectra from transient absorption measurements on the dyad in benzonitrile, and complete spectral data (¹H NMR, LD-MS) for all new compounds. This material is available free of charge via the Internet at http:// pubs.acs.org.

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