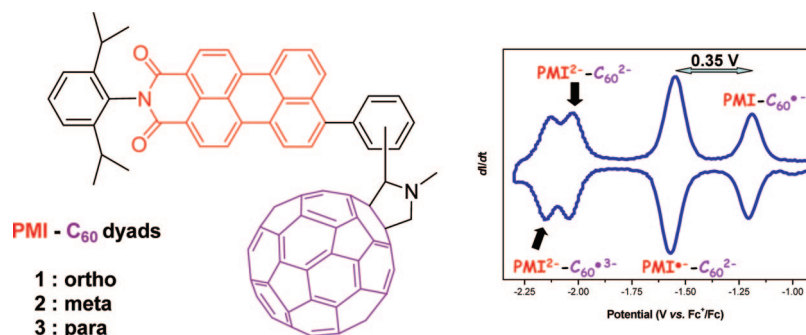# Synthesis of Perylene-3,4-mono(dicarboximide)−Fullerene C_{60} Dyads as New Light-Harvesting Systems

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Fullerene C_{60}−perylene-3,4-mono(dicarboximide) (C_{60}−PMI) dyads **1**−**3** were synthesized in the search for new light-harvesting systems. The synthetic strategy to the PMI intermediate used a cross-coupling Suzuki reaction for the introduction of a formyl group in the ortho, meta, or para position. Subsequent 1,3-dipolar cycloaddition with C_{60} led to the target C_{60}−PMI dyad. Cyclic voltammetry showed that the first one-electron reduction process unambiguously occurs onto the C_{60} moiety and the following two-electron process corresponds to the concomitant second reduction of C_{60} and the first reduction of PMI. A quasi-quantitative quenching of fluorescence was shown in dyads **1**−**3**, and an intramolecular energy transfer was suggested to occur from the PMI to the fullerene moiety. These C_{60}−PMI dyads constitute good candidates for future photovoltaic applications with expected well-defined roles for both partners, i.e., PMI acting as a light-harvesting antenna and C_{60} playing the role of the acceptor in the photoactive layer.

Introduction

In recent years, there has been an increasing interest in the design of new advanced materials using the perylene-3,4:9,10-bis(dicarboximide) (PDI) chromophore.[1] More recent applications are in the field of electronic materials, these dyes being considered as one of the more efficient n-type semiconductors now available.[2] Thanks to their unique light-harvesting, redox, and thermal stability properties, PDI dyes have been regarded as potential candidates for applications in xerography,[3] organic field-effect transistors,[4] organic light-emitting diodes,[5] and organic solar cells.[6] In the search for new organic materials devoted to photovoltaic applications, PDI was recently attached to fullerene C_{60} with the aim of reaching new light-harvesting systems **4** and **5** (Scheme 1).[7,8]

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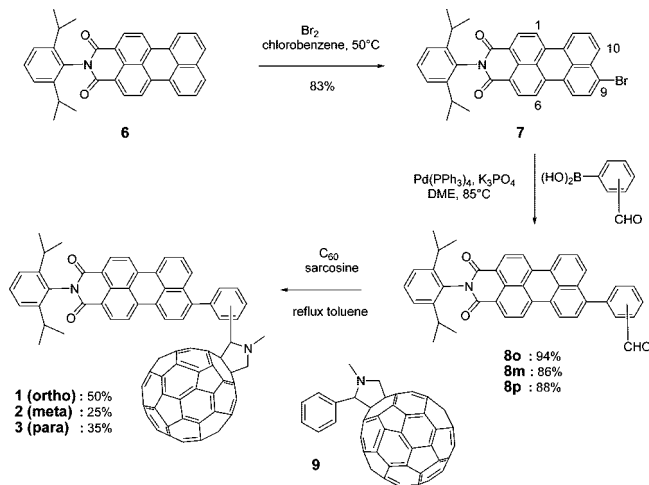(3) Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449–486.

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SCHEME 1. C$_{60}$−PMI dyads 1−3 and C$_{60}$−PDI Dyads 4 and 5

SCHEME 2. Synthesis of Dyads C$_{60}$−PMI 1−3
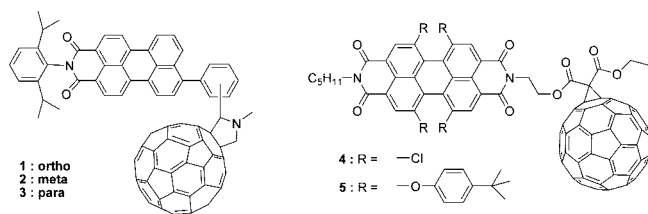
An efficient intramolecular energy transfer from the PDI toward fullerene C$_{60}$ was evidenced in dyads **4** and **5**.[9,10] Bulk-heterojunction solar cells were designed by mixing the donor polymer poly(3-hexylthiophene) with the C$_{60}$−PDI dyad considering that in the photoactive layer the dye should act as a light-harvesting antenna while an electron transfer should occur selectively from the p-type polymer to the C$_{60}$ unit.[11] Whereas it was reported in such dyads that C$_{60}$ and PDI are reduced at the same potential when PDI is substituted by hydrogen atoms ($\Delta E = E^1_{red}(C_{60}) - E^1_{red}(PDI) = 0$ mV),[8d] the electron-accepting character of PDI was shown to be affected by the introduction of electron-donating or -withdrawing groups at the PDI bay region (for R = Cl, $\Delta E = -240$ mV in dyad **4** and for R = OPh-*t*-Bu, $\Delta E = +140$ mV in dyad **5**) with a consequence on photovoltaic characteristics.[11]

Our following objective was to design new light-harvesting C$_{60}$ based systems in which (i) C$_{60}$ should be unambiguously the better electron acceptor ($\Delta E > 0$ mV) with a higher discrimination between the first reduction potential of C$_{60}$ and that of the dye and (ii) an efficient energy transfer should also occur from the antenna toward C$_{60}$. With this aim, we were interested in replacing the dye PDI by the less accepting dye perylene-3,4-mono(dicarboximide) (PMI). We report herein an efficient synthetic route to C$_{60}$−PMI dyads **1−3** and their electrochemical and spectroscopic properties (Scheme 2).

Whereas chemistry of PDI has been largely developed in recent years,[1,12] the synthesis of PMI derivatives has been less investigated. A series of donor−PMI systems have been reported in the literature in which PMI was attached to oligothiophene,[13] polyphenylene oligomers[14] or dendrimers,[15] based-tripheny-

lamine derivatives,[16] or zinc porphyrin[17] in the search of donor−acceptor electronic interactions. To our knowledge, PMI has never been attached to an acceptor such as fullerene C$_{60}$.[18]

Results and Discussion

Synthesis. The strategy for the synthesis of PMI−C$_{60}$ dyads **1−3** used the starting material *N*-(2,6-diisopropylphenyl)-perylene-3,4-mono(dicarboximide) **6**. The 9-bromo-PMI derivative **7** was synthesized by treating PMI **6** with bromine in chlorobenzene according to reported procedure.[19] Under our conditions, compound **7** was isolated in 83% yield and was accompanied by a small amount of the 1,6,9-tribominated derivative.[20] In our different attempts to optimize the yield in compound **7**, we could also isolate a mixture of 1,9- and 1,10-dibromo-PMI derivative (yield <5%). Subsequent palladium-catalyzed Suzuki-type cross-coupling of 9-brominated PMI **7** with commercially available formyl-substituted boronic acid in refluxing 1,2-dimethoxyethane (DME) overnight afforded in high yields 9-phenyl-PMI derivatives (**8o**: 94%; **8m**: 86%; **8p**: 88%). Using ultrasound conditions,[21] the Suzuki reaction time could be reduced to 3 h but yields remained lower (**8o**: 55%; **8m**: 63%; **8p**: 73%). The subsequent 1,3-dipolar cycloaddition[22]

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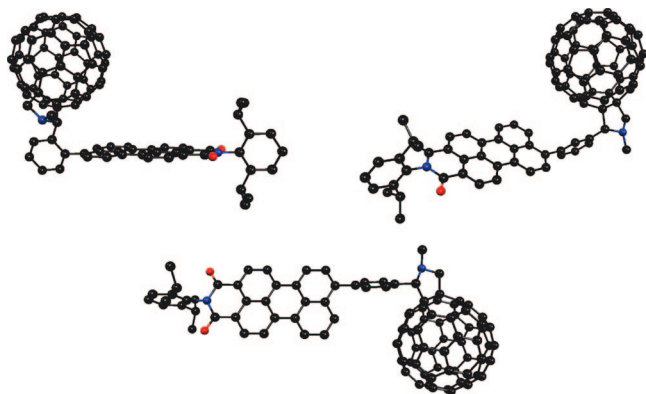
FIGURE 1. Optimized geometries of C_{60}−PMI dyads **1** (left), **2** (right), and **3** (bottom).

was carried out using C_{60} and *N*-methylglycine (sarcosine) in refluxing toluene affording, after purification by silica gel column chromatography, dyads **1**−**3** in satisfactory 25−50% yields. Subsequent purification of dyads **1**−**3** and references (PMI **6** and C_{60} derivative **9**) was carried out by analytical and semipreparative HPLC. The purity of dyads **1**−**3** could be estimated to be higher to 99.8%. Information on the steric interaction between PMI and C_{60} in solution is given by ^{1}H NMR spectra of dyads **1**−**3**. Whereas the four methyl groups (from both diisopropylphenyl groups) appear as a single doublet in the para derivative **3**, two and four doublets were observed in the case of the meta **2** and ortho **1** derivatives, respectively. Fulleropyrrolidine **9** was prepared in 40% yield by using benzaldehyde as the starting material to generate the azomethine ylide.[23]

Theoretical Calculations. Quantum chemical calculations on the three dyads **1**−**3** have been conducted to get further insights of molecular structure as well as molecular orbital energies. Geometrical optimization was performed with semiempirical methods using PM3 parametrization with Hyperchem 7.5. Electronic structures of optimized geometries were studied using the Gaussian 03 package with ab initio methods at the DFT level using the exchange correlation hybrid functional Becke3LYP with the atomic basis 6-31G(2d,p) for all atoms. The 2,6-diisopropylphenyl group is found to be nearly perpendicular to the planar perylene core, thus minimizing steric hindrance between isopropyl groups and the imide functionality (Figure 1). On the opposite part of these systems, the plane of the phenyl spacer is oriented out of the perylene plane. In agreement with expected values relative to the ortho, meta, or para substitution of the phenyl group, the shortest distance between the perylene core and C_{60} was determined to be 3.72, 4.51, and 5.28 Å for dyads **1**, **2**, and **3**, respectively. The shortest distance between the perylene core and C_{60} took into account the nearest (C_{10}) carbon atom of the perylene.

Cyclic Voltammetry. Cyclic voltammograms (CV) of all three dyads **1** (Figure 2), **2**, and **3** show four reversible reduction waves, with the first, third, and fourth ones corresponding to one-electron processes, while the second one corresponds to a two-electron process. By comparison with those of reference compounds **6** and **9** (Table 1), the first one-electron process is assigned to the formation of the anion radical of the C_{60} moiety (C_{60}•−−PMI). This result is in agreement with theoretical calculations of the energy levels of the HOMO and LUMO
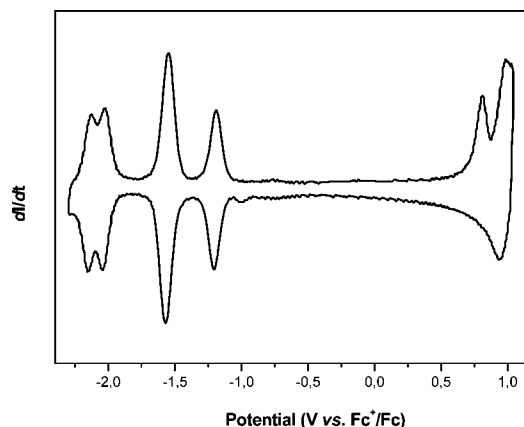
FIGURE 2. Deconvoluted cyclic voltammogram of dyad **1**. Experimental conditions are detailed in Table 1.

TABLE 1. Redox Potential Values (V vs Fc[+]/Fc) of PMI−C_{60} Dyads **1**−**3** and Reference Compounds **6** and **9**[a]

	E^4_{red}	E^3_{red}	E^2_{red}	E^1_{red}	E^1_{ox}	E^2_{ox}
1	−2.14	−2.03	−1.56[b]	−1.20	+0.81[c]	+0.98[d]
2	−2.12	−1.99	−1.55[b]	−1.19	+0.88[d]	
3	−2.11	−1.97	−1.55[b]	−1.20	+0.85[c]	+0.96[d]
6			−1.99	−1.54	+0.92[d]	
9		−2.09	−1.58	−1.21	+0.89[c]	

[a] Values recorded in a *o*-dichlorobenzene/CH_2Cl_2 (2:1) solution (5.10^{-4} M) using Bu_4NPF_6 0.1M as the supporting electrolyte, platinum wires as counter and working electrodes. Scan rate: 100 mV/s. [b] Two one-electron process; [c] Irreversible process; [d] Quasi-irreversible process.

orbitals which predicted that the LUMO of the system would be located on C_{60} whereas the HOMO would be on the PMI moiety. The following two-electron process corresponds to the generation of the C_{60}^{2-}−PMI•− species, suggesting that the second reduction process of C_{60} and the first reduction process of PMI are overlapping. Consequently, such an important difference ($\Delta E = E^1_{red}(C_{60}) - E^1_{red}(PMI) = +350$ mV) will make C_{60} the unambiguous electron acceptor when this dyad will be incorporated in a bulk-heterojunction device with the donor polymer.

The third and fourth one-electron waves result from the formation of C_{60}^{2-}−PMI[2−] and $C_{60}^{3\bullet-}$−PMI[2−] species, respectively. Due to the close proximity of oxidation potentials of C_{60} and PMI references (**9** and **6**), corresponding oxidation processes occurring in the dyads could not be formally ascribed. Moreover, comparison of these different values for dyads **1**, **2**, and **3** with reference compounds **6** and **9** suggests that no significant interaction takes place between both electroactive moieties in the ground state.

Absorption and Steady-State Fluorescence Emission. Absorption and steady-state fluorescence emissions of dyads **1**−**3** and reference compounds **6** and **9** in CH_2Cl_2 are collected in Table 2.

Compound **9** exhibits a typical UV−vis absorption profile of pyrrolidino−fullerene adducts with a strong absorption band at ca. 300−330 nm, a sharp absorption band characteristic of fullerene adducts at 430 nm, as well as a broadband around 500 nm and a longest wavelength absorption band corresponding to the 0→0 transition at ca. 700 nm (Figure 3).[24] PMI **6** used as the reference displays a strong $\pi-\pi^*$ transition band in the

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TABLE 2. Selected Photophysical Data of Dyads 1−3 and Reference Compounds 6 and 9 in CH$_2$Cl$_2$ at 298 K.

	absorption maxima		fluorescence		
	λ_{max} (nm)	ϵ (L · mol^{-1} · cm^{-1})	λ_{max} (nm)	Φ_{fluo}[b]	E^{0-0} (eV)
1	523	35300	543	6.8×10^{-3}	2.33
2	519	36800	554	2×10^{-3}	2.32
3	517	37500	560	12×10^{-3}	2.33
6	507	27200	544	0.98	2.39
9	325	21200			
	(430, 702)[a]	(2270, 232)	707	2.8×10^{-4}	1.76

[a] Other absorption bands and their corresponding epsilon values. [b] Determined using cresyl violet as a standard ($\Phi_f = 0.54$ at 20 °C in MeOH).
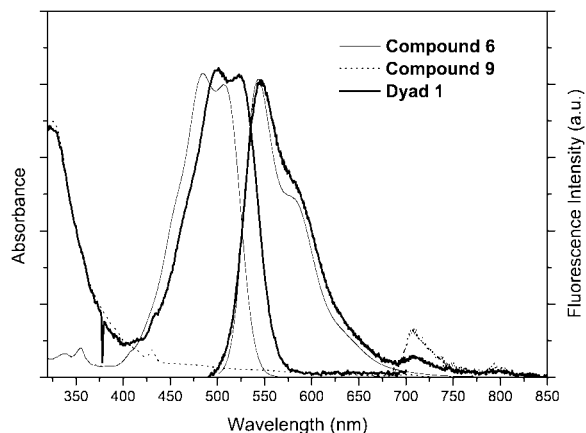

FIGURE 3. Absorption and fluorescence emission spectra of dyad **1** (bold line; λ_{exc} = 485 nm) and reference compounds **6** (full line; λ_{exc} = 485 nm) and **9** (dotted line; λ_{exc} = 325 nm) in CH$_2$Cl$_2$ at 298 K (c < 10^{-6} M).

visible range (corresponding to the 0→0 band at λ_{abs} = 507 nm and the comparably intense 0→1 band at λ_{abs} = 484 nm) as well as a very weak structured band at 355 nm and a last band (not shown) centered at 264 nm (Figure 3). Dyads **1−3** absorption spectra are composed of two distinct broad bands with the strong absorption of the C$_{60}$ moiety in the UV range and the $\pi-\pi^*$ transition band of the PMI moiety in the UV and visible range at ca. 520, 500, and 320 nm with high extinction coefficients (Figure 3). The orientation of C$_{60}$ toward PMI (ortho, meta, or para substitution pattern) seems to have no influence on the ground state as the three corresponding dyads have nearly the same absorption features.

Emission spectra of dyads **1−3** are characterized by a strong band corresponding to the 0→0 transition at ca. 540−560 nm. This band presents a shoulder at 570 nm which is attributed to the 1→0 transition band of the PMI emission. Another weak band around 700 nm characteristic of the 0→0 transition emission of fullerene was observed (Figure 3). An important quenching of fluorescence of the PMI moiety (superior to 98.5%) was observed in dyads **1−3** when compared to the fluorescence of compound **6**. This process must be intramolecular as the quantum yield of PMI **6** was not affected using a stoichiometric mixture of PMI **6** and fullerene **9** in concentration similar to the case of dyad **1−3**. By selectively exciting the PMI moiety in dyad **1**, at 525 nm, an emission from ^{1}C$_{60}^*$−PDI was still observed, giving evidence of a singlet−singlet energy transfer from the PMI moiety to C$_{60}$ moiety. This is in agreement with the energy levels of both units (2.39 eV for **6** and 1.76 eV for **9**). Competition with reductive electron transfer process can not be ruled out as the corresponding free energy ΔG_{PET} was found negative using the calculated "Gibbs energy of photoinduced electron transfer" (ΔG_{PET} = −0.32 eV for **1**,

ΔG_{PET} = −0.25 eV for **2**, ΔG_{PET} = −0.28 eV for **3**).[25] Photophysical investigations are underway in order to estimate the rate of energy transfer in these systems.

Conclusion

In conclusion, the synthesis and spectroscopic studies of C$_{60}$−perylene-3,4-mono(dicarboximide) dyads are described. It was clearly demonstrated that the PMI dye can act as a light-harvesting antenna for C$_{60}$ as previously shown for C$_{60}$−PDI dyads. Whereas in the latter case the first reduction potentials of C$_{60}$ and PDI are very close one to each other, the first reduction process unambiguously occurs on the C$_{60}$ moiety in the C$_{60}$−PMI dyads. Such C$_{60}$−PMI dyads absorb strongly in the visible range and could be good candidates for the development of efficient bulk-heterojunction photovoltaic devices by mixing with a p-type polymer donor.

Experimental Section

General Procedure for 1,3-Dipolar Cycloaddition. To a solution of *N*-(2,6-diisopropylphenyl)-9-(2-formylphenyl)perylene-3,4-dicarboximide **8o** (100 mg; 0.17 mmol) in anhydrous toluene (50 mL) were added C$_{60}$ (185 mg; 0.26 mmol) and *N*-methylglycine (sarcosine) (30 mg; 0.34 mmol). The reaction mixture was refluxed under nitrogen for 24 h. After the solution was cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. After elution with CS$_2$ to remove excess and unreacted C$_{60}$, dyad PMI−C$_{60}$ **1** was isolated as a reddish powder using CH$_2$Cl$_2$ as the eluent (113 mg, 50% yield).

***N*-(2,6-Diisopropylphenyl)-9-[2-(*N*-methyl-3,4-fulleropyrrolidi-nyl)phenyl]perylene-3,4-dicarboximide 1.** ^{1}H NMR (CS$_2$/CDCl$_3$ 3:1, 500 MHz) δ (ppm) 8.70 (d, ^3J = 8 Hz, 1H), 8.66 (d, ^3J = 8 Hz, 1H), 8.61 (d, ^3J = 8 Hz, 1H), 8.56 (d, ^3J = 8 Hz, 1H), 8.42 (d, ^3J = 8 Hz, 1H), 8.36 (d, ^3J = 8 Hz, 1H), 8.24 (d, ^3J = 8 Hz, 1H), 7.76−7.70 (m, 2H), 7.66 (t, ^3J = 8 Hz, 1H), 7.52 (dt, ^3J = 8 Hz and ^4J = 1 Hz, 1H), 7.48 (d, ^3J = 8 Hz, 1H), 7.40 (dd, ^3J = 8 Hz and ^4J = 1 Hz, 1H), 7.34 (d, ^3J = 8 Hz, 1H), 7.33 (t, ^3J = 8 Hz, 1H), 7.30 (d, ^3J = 8 Hz, 1H), 4.76 (d, ^3J = 9.4 Hz, 1H), 4.66 (s, 1H), 3.82 (d, ^2J = 9.4 Hz, 1H), 2.77 (s, 3H), 2.73 (hept, ^3J = 7 Hz, 2H), 1.19, 1.17, 1.16, 1.14 (4 d, ^3J = 7 Hz, 12H); IR (KBr, cm^{-1}) ν 2964, 2929, 1703, 1657, 1582, 1358, 1092, 1022, 977, 810 cm^{-1}; MS (MALDI-TOF, dithranol) 1332 (M)$^{+•}$, 612 (M − C$_{60}$); HR-MS (ESI) calcd for C$_{103}$H$_{37}$N$_2$O$_2$ 1333.2855, found 1333.2851.

***N*-(2,6-Diisopropylphenyl)-9-[3-(*N*-methyl-3,4-fulleropyrrolidi-nyl)phenyl]perylene-3,4-dicarboximide 2.** yield = 25%; ^{1}H NMR (CS$_2$/CDCl$_3$ 3:1, 500 MHz) δ (ppm) 8.60 (d, ^3J = 8 Hz, 1H), 8.59 (d, ^3J = 8 Hz, 1H), 8.51 (br d, ^3J = 8 Hz, 1H), 8.48 (d, ^3J = 8 Hz, 1H), 8.44 (d, ^3J = 8 Hz, 1H), 8.42 (br d, ^3J = 8 Hz, 1H), 8.30−7.80 (br m, 3H), 7.66−7.54 (br m, 3H), 7.51 (br d, ^3J = 8 Hz, 1H), 7.42 (t, ^3J = 7.5 Hz, 1H), 7.31 (s, 1H), 7.27 (d, ^3J = 8 Hz, 1H),

(25) Rehm, D.; Weller, A. *Isr. J. Chem* **1970**, *8*, 259−271.

5.08 (s, 1H), 5.01 (br d, ^2J = 9.5 Hz, 1H), 4.34 (d, ^2J = 9.5 Hz, 1H), 2.92 (br s, 3H), 2.69 (hept, ^3J = 7 Hz, 2H), 1.15 and 1.16 (2 d, ^3J = 7 Hz, 12H); IR (KBr, cm^{-1}) ν 2964, 2929, 1702, 1651, 1571, 961, 810 cm^{-1}; MS (MALDI-TOF, dithranol) 1333 (M + H)$^+$, 612 (M − C$_{60}$); HR-MS (ESI) calcd for C$_{103}$H$_{37}$N$_2$O$_2$ 1333.2855, found 1333.2848.

N-(2,6-Diisopropylphenyl)-9-[4-(N-methyl-3,4-fulleropyrrolidinyl)phenyl]perylene-3,4-dicarboximide 3. yield = 35%; ^{1}H NMR (CS$_2$/CDCl$_3$ 3:1, 500 MHz) δ (ppm) 8.60 (d, ^3J = 8 Hz, 2H), 8.50 (d, ^3J = 8 Hz, 1H), 8.47 (m, 3H), 8.01 (broad s, 2H), 7.87 (broad d, 1H), 7.62−7.55 (m, 4H), 7.42 (t, ^3J = 8 Hz, 1H), 7.27 (d, ^3J = 8 Hz, 1H), 7.26 (s, 1H), 5.10 (s, 1H), 5.06 (d, ^2J = 9.2 Hz, 1H), 4.37 (d, ^2J = 9.2 Hz, 1H), 2.96 (s, 3H), 2.69 (hept, ^3J = 7 Hz, 2H), 1.16 (d, ^3J = 7 Hz, 12H); ^{13}C NMR (CS$_2$/CDCl$_3$ (3:1)) δ (ppm) 144.86, 144.44, 144.28, 144.12, 144.03, 142.91, 142.78, 142.45, 142.37, 142.34, 142.29, 141.95, 141.89, 141.88, 141.79, 141.67, 141.66, 141.51, 141.43, 141.32, 140.01, 139.98, 139.74, 139.70, 139.12, 136.96, 136.76, 136.72, 136.21, 135.71, 135.41, 132.37, 131.57, 130.77, 130.25, 130.09, 129.27, 128.97, 128.80, 128.52, 128.23, 128.04, 126.87, 126.65, 123.60, 123.53, 123.18, 121.05, 120.98, 120.21, 119.98, 83.00, 76.87, 69.83, 68.67, 39.86, 29.83, 28.96, 23.81; IR (KBr, cm^{-1}) ν 2930, 1703, 1657, 1545, 1358, 969 cm^{-1}; MS (MALDI-TOF, dithranol) 1331 (M − H)$^+$, 612 (M − C$_{60}$); HR-MS (ESI) calcd for C$_{103}$H$_{37}$N$_2$O$_2$ 1333.2855, found 1333.2837.

N-(2,6-Diisopropylphenyl)-9-bromoperylene-3,4-dicarboximide 7. N-(2,6-Diisopropylphenyl)perylene-3,4-dicarboximide (5 g, 10.5 mmol) were dissolved in chlorobenzene (500 mL). Bromine (2.40 mL, 47.5 mmol) was added, and the reaction mixture was stirred for 5 h at 50 °C. Unreacted bromine was removed using nitrogen flow, and chlorobenzene was removed under reduced pressure. The residue was purified by column chromatography on silica gel using CH$_2$Cl$_2$ as the eluent affording compound 7 (4.8 g; 83% yield) and the 1,6,9-tribromoperylene-3,4-dicarboximide derivative (1.28 g; 17%) as reddish powders. Both compounds were recrystallized using CHCl$_3$/methanol as the mixture of eluents: ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm): 8.68 (d, ^3J = 7 Hz, 1H), 8.65 (d, ^3J = 7 Hz, 1H), 8.56 (d, ^3J = 8 Hz, 1H), 8.50 (d, ^3J = 8 Hz, 1H), 8.45 (d, ^3J = 8 Hz, 1H), 8.36 (d, ^3J = 8 Hz, 1H), 8.30 (d, ^3J = 8 Hz, 1H), 7.96 (d, ^3J = 8 Hz, 1H), 7.76 (t, ^3J = 8 Hz, 1H), 7.50 (t, ^3J = 8 Hz, 1H), 7.35 (d, ^3J = 8 Hz, 2H), 2.74 (hept, ^3J = 7 Hz, 2H), 1.18 (s, ^3J = 7 Hz, 12H); IR (KBr, cm^{-1}) ν 2976, 1701, 1659, 1591, 1562, 1359, 1247, 837, 805, 751 cm^{-1}; MS (MALDI-TOF, dithranol) 560/562 (M + H)$^+$.

N-(2,6-Diisopropylphenyl)-1,6,9-tribromoperylene-3,4-dicarboximide. ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm) 9.40 (d, ^3J = 7.5 Hz, 1H), 9.10 (d, ^3J = 7.5 Hz, 1H), 8.98 and 8.97 (2 s, 2H), 8.45 (d, ^3J = 8 Hz, 1H), 8.00 (d, ^3J = 8 Hz, 1H), 7.80 (t, ^3J = 8 Hz, 1H), 7.50 (t, ^3J = 7 Hz, 1H), 7.35 (d, ^3J = 7 Hz, 2H), 2.75 (hept, ^3J = 7 Hz, 2H), 1.20 (d, ^3J = 7 Hz, 12H); MS (MALDI-TOF, dithranol) 719 (M + H)$^+$.

General Procedure for the Suzuki Cross-Coupling Reaction. Classical Conditions. To a solution of compound 7 (100 mg; 0.17 mmol) in dry 1,2-dimethoxyethane (DME or glyme) (20 mL) were added under nitrogen 2-formylphenylboronic acid (32 mg; 0.22 mmol) and potassium phosphate tribasic (K$_3$PO$_4$) (100 mg; 0.47 mmol) followed by Pd(PPh$_3$)$_4$ (20 mg; 16 μmol). The reaction mixture was refluxed for 15 h. After being cooled to room temperature, the solution was poured into water (50 mL) and extracted with CH$_2$Cl$_2$ (3 × 30 mL). The combined organic phases were washed with water (2 × 30 mL), dried over MgSO$_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel by using CH$_2$Cl$_2$ as the eluent affording compound 8o as a reddish powder (98 mg; 94% yield).

Under Ultrasound Conditions. To a solution of compound 7 (50 mg; 0.089 mmol) in dry DME (10 mL) were added under nitrogen 2-formylphenylboronic acid (16 mg; 0.11 mmol) and potassium phosphate tribasic (K$_3$PO$_4$) (46 mg; 0.22 mmol) followed by Pd(PPh$_3$)$_4$ (12 mg; 10 μmol). The reaction mixture was stirred

under ultrasound for 13 h. After being cooled to room temperature, the solution was poured in water (50 mL) and extracted with CH$_2$Cl$_2$ (3 × 30 mL). The combined organic phases were washed with water (2 × 30 mL), dried over MgSO$_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel by using CH$_2$Cl$_2$ as the eluent affording compound 8o as a reddish powder (29 mg; 55% yield).

N-(2,6-Diisopropylphenyl)-9-(2-formylphenyl)perylene-3,4-dicarboximide 8o. yield = 94%; ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm) 9.78 (s, 1H), 8.68 (d, ^3J = 8 Hz, 1H), 8.66 (d, ^3J = 8 Hz, 1H), 8.53 (d, ^3J = 8 Hz, 1H), 8.50 (d, ^3J = 8 Hz, 1H), 8.49 (d, ^3J = 8 Hz, 1H), 8.47 (d, ^3J = 8 Hz, 1H), 8.17 (dd, ^3J = 7.5 Hz and ^4J = 1 Hz, 1H), 7.78 (dt, ^3J = 7.5 Hz and ^4J = 1 Hz, 1H), 7.67 (t, ^3J = 7.5 Hz, 1H), 7.61 (d, ^3J = 8 Hz, 1H), 7.59 (d, ^3J = 8 Hz, 2H), 7.53 (d, ^3J = 7.5 Hz, 1H), 7.49 (t, ^3J = 8 Hz, 1H), 7.36 (d, ^3J = 8 Hz, 2H), 2.74 (hept, ^3J = 7 Hz, 2H), 1.20 (d, ^3J = 7 Hz, 12H); ^{13}C NMR (CDCl$_3$) δ (ppm) 191.43, 163.91, 145.73, 145.68, 142.97, 138.69, 137.29, 137.05, 134.87, 133.98, 133.83, 132.07, 132.05, 131.58, 130.98, 130.48, 129.61, 129.46, 129.23, 128.86, 128.81, 128.05, 127.73, 126.93, 124.05, 124.04, 124.00, 122.93, 121.35, 121.29, 120.65, 120.47, 29.69, 29.15, 24.02; IR (KBr, cm^{-1}) ν 2964, 2933, 1702, 1657, 1593, 1571, 1359, 1092, 1023, 810 cm^{-1}; MS (MALDI-TOF, dithranol) 586 (M)$^{+•}$.

N-(2,6-Diisopropylphenyl)-9-(3-formylphenyl)perylene-3,4-dicarboximide 8m. 86% yield for classical procedure and 63% yield using ultrasound conditions; ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm) 10.16 (s, 1H), 8.69 (d, ^3J = 8 Hz, 1H), 8.67 (d, ^3J = 8 Hz, 1H), 8.54 (d, ^3J = 8 Hz, 1H), 8.51 (d, ^3J = 8 Hz, 1H), 8.50 (d, ^3J = 8 Hz, 1H), 8.49 (d, ^3J = 8 Hz, 1H), 8.08 (s, 1H), 8.03 (d, ^3J = 8 Hz, 1H), 7.90 (d, ^3J = 8 Hz, 1H), 7.84 (d, ^3J = 8 Hz, 1H), 7.75 (t, ^3J = 8 Hz, 1H), 7.63 (t, ^3J = 8 Hz, 1H), 7.62 (d, ^3J = 8 Hz, 1H), 7.49 (t, ^3J = 8 Hz, 1H), 7.35 (d, ^3J = 8 Hz, 2H), 2.78 (hept, ^3J = 7 Hz, 2H), 1.19 (d, ^3J = 7 Hz, 12H); ^{13}C NMR (CDCl$_3$) δ (ppm) 191.99, 163.96, 145.72, 141.56, 140.87, 137.51, 137.24, 136.77, 135.85, 132.47, 132.08, 131.01, 130.93, 130.51, 129.58, 129.46, 129.41, 129.37, 129.20, 128.68, 128.39, 127.41, 126.93, 124.02, 123.40, 121.14, 120.52, 120.34, 29.14, 24.01; IR (KBr, cm^{-1}) ν 2972, 1702, 1657, 1545, 1360, 969, 814, 749 cm^{-1}; MS (MALDI-TOF, dithranol) 586 (M)$^{+•}$.

N-(2,6-Diisopropylphenyl)-9-(4-formylphenyl)perylene-3,4-dicarboximide 8p. 88% yield for classical procedure and 73% yield using ultrasound conditions; ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm) 10.14 (s, 1H), 8.70 (d, ^3J = 8 Hz, 1H), 8.69 (d, ^3J = 8 Hz, 1H), 8.55 (t, ^3J = 8 Hz, 1H), 8.54 (d, ^3J = 8 Hz, 1H), 8.52 (d, ^3J = 8 Hz, 1H), 8.51 (d, ^3J = 8 Hz, 1H), 8.09 (d, ^3J = 8 Hz, 2H), 7.94 (d, ^3J = 8 Hz, 1H), 7.74 (d, ^3J = 8 Hz, 2H), 7.64 (t, ^3J = 8 Hz, 2H), 7.49 (t, ^3J = 8 Hz, 1H), 7.35 (d, ^3J = 8 Hz, 2H), 2.77 (hept, ^3J = 7 Hz, 2H), 1.19 (d, ^3J = 7 Hz, 12H); ^{13}C NMR (CDCl$_3$) δ = 191.75, 163.91, 146.09, 145.68, 141.64, 137.41, 137.11, 135.80, 132.23, 132.03, 132.02, 130.96, 130.71, 130.44, 129.95, 129.53, 129.45, 129.33, 128.66, 128.36, 128.23, 127.40, 126.86, 124.03, 124.00, 123.30, 121.17, 121.13, 120.50, 120.34, 29.13, 23.98; IR (KBr, cm^{-1}) ν 2972, 2929, 1703, 1657, 1579, 1360, 969 cm^{-1}; MS (MALDI-TOF, dithranol) 586 (M)$^{+•}$.

N-Methyl-2-phenyl-3,4-fulleropyrrolidine 9. To a solution of C$_{60}$ (100 mg; 0.14 mmol) in dry toluene (100 mL) were added benzaldehyde (20 μL; 0.2 mmol) and sarcosine (13 mg; 0.15 mmol). The reaction mixture was stirred at 90 °C for 8 h under nitrogen. After being cooled to room temperature, the solution was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel by using CS$_2$ as the eluent to afford compound 9 as a black powder (47 mg; 40% yield): ^{1}H NMR (CS$_2$/CDCl$_3$ 3:1), 500 MHz) δ (ppm) 7.78 (br m, 1H), 7.41 (t, ^3J = 7.5 Hz, 1H), 7.33 (t, ^3J = 7.5 Hz, 1H), 7.18 (d, ^3J = 7.5 Hz, 1H), 7.10 (d, ^3J = 7.5 Hz, 1H), 4.99 (d, ^2J = 9.5 Hz, 1H), 4.94 (s, 1H), 4.29 (d, ^2J = 9.5 Hz, 1H), 2.84 (s, 3H); IR (KBr, cm^{-1}) ν 2933, 1073, 1023, 969, 702 cm^{-1}; MS (MALDI-TOF, dithranol) 852 (M − H)$^+$.

Steady-State Spectroscopy. All solvents used are spectroscopic grade and were used as commercially available. Electronic absorp-

tion spectra were recorded with a Lambda 19 NIR model from Perkin-Elmer. Fluorescence spectra were recorded in nondeoxygenated solvents at 20 °C with a QM-4/QuantaMaster fluorometer from PTI equipped with rapid monochannel detection and continuous excitation source. Quantum yields were determined using cresyl violet as a standard reference ($\Phi_f = 0.54$ at 20 °C in MeOH).[26]

Cyclic Voltammetry. Cyclic voltammetry was performed in a three-electrode cell equipped with a platinum millielectrode and a platinum wire counter-electrode. A silver wire served as pseudo-reference electrode, and its potential was checked against the ferricinium/ferrocene couple (Fc^+/Fc) before and after each experiment. The electrolytic media involved CH_2Cl_2 (HPLC grade), *o*-dichlorobenzene (Aldrich spectroscopic grade), and 0.1 M of tetrabutylammonium hexafluorophosphate (TBAHP, puriss quality).

All experiments were performed in a glovebox containing dry, oxygen-free (<1 ppm) argon, at room temperature. Electrochemical experiments were carried out with an EGG PAR 273A potentiostat.

Supporting Information Available: Spectroscopic and photophysical data for all new molecules synthesized, CVs of dyads **1−3**, and reference numbers **6** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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