Synthesis of Perylene Dyes with Multiple Triphenylamine Substituents

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Abstract: Perylene monoimide (PMI) was brominated to give tetra- and tribrominated molecules, which underwent a Suzuki coupling reaction with 4- (diphenylamino)phenylboronic acid to give PMI derivatives. The photophysical and electrochemical properties of the synthesized compounds were investigated, and theoretical calculations were performed. Single crystals of tet-

rasubstituted PMI were grown and studied in detail. The structure-property relationships were examined to reveal the effect of the position and number of substituents on the perylene

Keywords: density functional calculations • dyes/pigments • polycycles • solar cells • substituent effects

core unit. All molecules showed a broad absorption up to 750 nm. Corresponding anhydrides of PMIs were used for fabrication of dye-sensitized solar cells. The molecule with four triphenylamine units on perylene monoanhydride showed the highest power conversion efficiency.

with a wide absorption range covering most of the solar spectrum up to the NIR region is interesting and used in the current investigation.^[2b,5f,11] Triphenylamine (TPA) is known to be an efficient donor moiety that interacts electronically with the perylene core to produce interesting intramolecular charge transfer (ICT).^[11] Herein, the design and synthesis of a series of TPA-functionalized pervlene monoanhydrides (PMAs) from multibrominated perylene monoimides (PMIs) is reported. The effects of the number and steric crowding of TPA groups and overall conformation of the PMI molecules on the photophysical and electrochemical properties are investigated. Good-quality single crystals of the four TPA-incorporated PMIs were grown and analyzed to understand the influence of steric crowding on the conformation and lattice packing of such a big molecule. Careful separation of regioisomers of perylene is a key step involved in synthesizing target molecules.

Results and Discussion

The molecular structures of all synthesized target compounds are given in Scheme 1. In compound 8, the TPA units are attached to the PMA moiety through the 1,6,9 positions, whereas TPA is attached at the 1,9,10 positions in compound 9 and the 1,6,9,10 positions in compound 10, thus leading to incorporation of multiple donors into a single acceptor unit. All compounds have been isolated, purified, and fully characterized.

Syntheses of target compounds were achieved through the following route. *N*-(2-Ethylhexyl)perylene-3,4-dicarboximide (1) was synthesized from 3,4,9,10-perylenetetracarboxylic acid anhydride (PDA) by partial decarboxylation following a modified procedure reported earlier.^[12] The selective bromination of the N-substituted (aryl/alkyl)perylene-3,4-dicarboximides was reported with bromine in chlorobenzene and methylene chloride to give monobromination at the 9 posi-

Introduction

Recently, the design and synthesis of advanced materials with the perylene chromophore has been an active area of research.^[1] Unique light-harvesting and redox properties combined with high thermal stabilities of perylene dyes offer potential applications in organic field-effect transistors,^[2] xerography,^[3] organic light-emitting diodes.^[4] and photovoltaic devices.^[5] In metal-free dyes, perylene derivatives have been widely applied in various optical devices,^[6] light-harvesting arrays, and photosynthetic systems.^[7] More recently, perylene-based dyes were used in biological applications.^[8] A rising interest is to use ruthenium-free dyes as sensitizers for dye-sensitized solar cells (DSSCs),^[9] because such dyes hold many advantages over ruthenium-based dyes such as a higher absorption coefficient, lower cost, and ease of tuning molecular energy levels. However, to obtain a single sensitizer that is capable of effectively capturing light over the entire spectrum from the visible to near-infrared (NIR) region and simultaneously fulfills all the requirements for an efficient device remains a challenge.^[10]

The strategy of incorporating multiple donor moieties on to the single acceptor moiety to obtain a stable, soluble dye

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Scheme 1. Synthesis of functionalized PMI and PMA compounds.

tion,^[13,14] and bromination under reflux conditions in chloroform gave threefold bromination at the 1,6,9 positions of *N*arylPMI.^[11a,12,13c,14,15] In this study, the bromination of *N*-(2ethylhexyl)perylene-3,4-dicarboximide in chloroform under reflux conditions gave tetrabromo- and tribromoPMI in good yields. The crude brominated PMI showed two spots on a thin-layer chromatography (TLC) plate with a mixture of dichloromethane and hexane (1:1). The crude mixture was purified by column chromatography and the ¹H NMR spectrum of the compound with an R_f value of 0.78 showed two sets of peaks, which are assigned to 1,6,9,10-tetrabromoPMI (4) and 1,6,9-tribromoPMI (2); MALDI-TOF analysis also confirmed the presence of both compounds.

The ¹H NMR spectrum of a second compound with an R_f value of 0.74 was assigned to 1,9,10-tribromoPMI (**3**). It was found that the solubility of tribromo- and tetrabromoPMI derivatives varies in common solvents. Repetitive precipitation from hexane gave pure tetrabromoPMI, which was

used for further characterization. From the ¹H NMR analysis of the crude mixture, the mole ratio of compounds 2-4 was found to be 4:2:1, respectively.

The syntheses of TPA-substituted PMI compounds 5-7 are depicted in Scheme 1. The brominated crude mixture was reacted with 4-(diphenylamino)phenylboronic acid by the Suzuki coupling reaction to obtain compounds 5-7. These compounds were successfully purified by column chromatography and were then characterized.

Alkaline treatment of compounds 5-7 with KOH/tBuOH afforded the target PMAs 8-10, respectively. All molecules were highly soluble in common organic solvents, such as dichloromethane, chloroform, and tetrahydrofuran (THF).

Single crystals of tetra-TPA-substituted PMI (7) were obtained by slow diffusion of hexane into a solution of the compound in chloroform. The molecules were packed in triclinic space group $P\overline{1}$. The asymmetric unit contains one tetra-TPA-substituted PMI (7) molecule and two chloroform molecules. Two molecules of compound 7 form a dyad in a head-to-tail fashion through strong $\pi - \pi$ interactions (Figure 1) with a separation of 3.81 Å. In the crystal structure, two naphthalene units of the perylene moiety are distorted to an angle of 21.5° from planarity owing to the presence of bulky TPA substitution at the 1 and 6 positions of the perylene core (bay positions). The individual benzene rings of the naphthalene unit away from the imide group are further distorted to an angle of 30° due to the steric hindrance from substitution at the 9 and 10 positions of the perylene core (peri positions). The TPA groups interact with molecules in the adjacent lattice to fill up the volume and molecules are packed in an ABC pattern (Figures S6 and S7 in the Supporting Information). No strong interactions are observed among the phenyl groups of the TPA units from the adjacent molecules.

The absorption spectra of PMA dyes in chloroform are shown in Figure 2B. The broader absorption between 400 and 750 nm is attributed to an extended conjugation and photoinduced ICT absorption of the perylene dye, which results from the orbital partitioning induced from substitution of TPA on the perylene core.^[11a-c] This ICT absorption band was clearly visible in the case of TPA-substituted perylene diimide systems.^[11d,e] Compared to the trisubstituted PMAs, tetrasubstituted PMA (10) shows broad absorption up to with a high extinction 750 nm coefficient of $56600 \,\mathrm{m}^{-1} \mathrm{m}^3 \mathrm{cm}^{-1}$. Compound 9 showed slightly broader ab-



dyes in CHCl₃ were acquired by excitation at their respective λ_{max} , and are presented in Figure 2 and summarized in Table 1. As expected the emission intensity was significantly lower in all cases compared with unsubstituted PMI.^[16] This can be rationalized by intramolecular electron-transfer processes and vibrational relaxation

The emission spectra of PMA

Figure 1. A) Crystal structure of compound 7, B) dyad formation, and C) schematic view of the dyad.

1.2 400 1.0 300 Normalized Absorbance 0.8 Emission Intensity 0.6 200 0.4 100 0.2 0.0 650 550 450 500 600 750 400 700 800 Wavelength (nm) 250 1.2 10 в 1.0 200 Vormalized Absorbance 0.8 Emission Intensity 0.6 100 0.4 50 0.2 0.0 500 550 600 650 700 400 450 750 800 Wavelength (nm)

Figure 2. Absorption (solid lines) and emission (dotted lines) spectra of PMI (A) and PMA (B) compounds (10⁻⁵ м) in chloroform at room temperature.

sorption than 8, which indicates that the substitution at the peri position improves the ICT absorption. The same trend was also observed for the PMI compounds 5-7 with a blueshift on λ_{max} values relative to their respective PMA dyes. The absorption spectra of compounds 5 and 6 were similar, with no influence from the position of substituents in these tri-TPA-substituted compounds. All three PMA dyes displayed broader absorption properties across the visible region of the spectrum.

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Table 1. Summary of photophysical and electrochemical properties of TPA–PMI/ $\ensuremath{\mathsf{PMA}}$ dyes.

Compound	$\lambda_{\max}^{[a]}$ [nm]	$\lambda_{em}^{[a]}$ [nm]	$E_{\mathrm{ox}}^{[\mathrm{b}]}$ [V]	$E_{\rm red}^{\rm [b]}$ [V]	HOMO ^[c] [eV]	LUMO ^[d] [eV]	$E_{g}^{[e]}$ [eV]
5	576, 483	667	0.42, 0.52, 0.90	-1.34	-5.22	-3.46	1.76
6	582, 477	679	0.47, 0.59, 0.93	-1.35	-5.25	-3.45	1.80
7	608, 497	700	0.40, 0.60, 0.97	-1.39	-5.20	-3.41	1.79
8	582, 488	695	0.35, 0.54, 0.98	-1.30	-5.15	-3.50	1.65
9	595, 488	714	0.33, 0.53, 0.97	-1.29	-5.13	-3.51	1.62
10	624, 515	721	0.37, 0.56, 1.01	-1.27	-5.14	-3.53	1.61

[a] Recorded in chloroform. [b] Versus ferrocene in $0.1 \text{ M Bu}_4\text{NPF}_6$ in dichloromethane, with a platinum disk as the working electrode and a scan rate of 100 mV s^{-1} . [c] Calculated by using the relationship $E_{\text{HOMO}} = -(E_{\text{oxs}}^{\text{onset}} + 4.8)$. [d] Calculated by using the relationship $E_{\text{LUMO}} = -(E_{\text{red}}^{\text{onset}} + 4.8)$. [e] Electrochemical bandgap.

upon substitution of electron-donating TPA groups on the electron-deficient perylene core.^[5f,11a,d] The emission maximum of **8** appeared at 695 nm. The introduction of the TPA moiety at the 9 and 10 positions of perylene resulted in a bathochromic shift of the emission maxima to 714 and 721 nm for compounds **9** and **10**, respectively. In the case of compounds **6** and **7**, a significant difference in emission maximum was observed (21 nm). A significant redshift in emission maximum was noticed for *peri*-substituted over bay-substituted compounds.

The electrochemical properties were investigated by cyclic voltammetry and all PMA and PMI dyes showed ambipolar redox behavior (Figure 3 and Figure S1 in the Supporting Information). During the positive potential sweep, all dyes showed three reversible oxidation peaks, for which the first and second oxidation potentials were assigned to the oxidation of TPA.^[11d] The third oxidation peak may correspond to perylene core oxidation.^[13d] In the negative potential regime, only one characteristic reduction wave of the perylene moiety was observed.^[11a] This was also supported by theoretical calculations. The HOMO and LUMO energy levels were determined from the oxidation and reduction onset potentials (Table 1). Interestingly, dyes **8–10** possess a

similar energy gap (E_g) as the positions of the HOMO and LUMO levels were not significantly different.

To gain further insight into the geometric, electronic, and optical properties of pervlene dyes, hybrid density functional theory (DFT) at the B3LYP level with 6-31G(d) as the basis set was used for geometry and energy optimization. The optimized structures of the respective molecules and the distribution of frontier orbitals were calculated (Figure 4, Figures S2 and S3 in the Supporting Information). Surprisingly, the HOMOs of PMA/PMI dyes are distributed on the TPA substituents as well as on the perylene core, whereas the LUMOs are seen on the perylene core and on the anhydride moiety, as expected. The calculated HOMO and LUMO energy values were found to be slightly higher, also as expected, and this trend was in agreement with experimental values.^[11a-d] The twisting angle (θ) of the perylene core of the molecules **8–10** was different (Table 2). In the case of compound **7**, the twisting angle was 22°, which is in agreement with single-crystal data.

In a preliminary test, DSSCs were fabricated by immersing TiO_2 electrodes in solutions of compounds **8–10** in THF. The electrode had a doublelayer structure consisting of a 12 µm thick transpar-

ent layer with 20 nm TiO_2 nanoparticles and a 4 μ m thick scattering layer of 400 nm TiO_2 nanoparticles. The electrodes were immersed in a 0.25 mM solution (THF) and left overnight before being removed and rinsed in THF immediately before cell assembly. Photoanodes and platinized coun-



Figure 3. Cyclic voltammograms of PMA dyes **8–10** in $0.1 \text{ M Bu}_4\text{NPF}_6$ in dichloromethane, with a platinum disk as working electrode at a scan rate of 100 mV s^{-1} in dichloromethane. Fc/Fc⁺ = ferrocene/ferrocenium.



Figure 4. The optimized geometric structures of TPA–PMA dyes and their frontier orbitals were calculated by DFT at the B3LYP/6-31G(d) level.

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Table 2. Theoretically calculated data of synthesized PMI/PMA dyes.

Compound	HOMO [eV]	LUMO [eV]	E_{g} [eV]	Twisting angle $[\theta]$
1	-5.49	-2.77	2.72	0
5	-4.84	-2.58	2.26	21
6	-4.87	-2.61	2.26	17
7	-4.76	-2.58	2.18	22
8	-4.95	-2.77	2.18	23
9	-4.98	-2.80	2.18	17
10	-4.87	-2.74	2.13	22

ter electrodes were sealed together in a sandwich configuration and were filled with an electrolyte (1 M propylmethylimidazolium iodide, 0.1 M I_2 , 0.1 M lithium bis(trifluoromethane)sulfonamide, and 0.5 M *N*-methylbenzimidazole) by vacuum back-filling. The current-voltage (*I*-*V*) characteristics and power conversion efficiencies (η) were evaluated for all three PMA dyes under simulated air mass (AM) 1.5 illumination and are presented in Figure 5 and Table 3.



Figure 5. I-V characteristics of solar cells of TPA–PMA dyes under AM 1.5 illumination.

Table 3.	I-V	data	of	TPA-	-PMA	dyes

Compound	$J_{ m sc}$ [mA cm ⁻²]	$V_{ m oc}$ [V]	η [%]	Fill factor [%]
8	2.22	0.59	0.95	69.5
9	2.07	0.57	0.85	69.0
10	3.08	0.53	1.14	66.8

The low power conversion was on account of lower current density (J_{sc}) values, which may be due to insufficient dye loading on the electrodes, even though the dyes showed broad absorption spectra. The open-circuit voltage (V_{oc}) values were not optimized and slightly lower than reported values.^[11a] The current values and efficiencies could be improved by 1) increasing the dye loading on TiO₂ by incorporating solubilizing groups on the molecule, 2) optimizing the performance of the electrolyte and electrodes, and 3) lowering the bulkiness of the substituents at the bay position.

Conclusion

FULL PAPER

We have synthesized highly stable and soluble TPA-incorporated PMA dyes with interesting architectures. The number and positions of TPA units on PMI/PMA were studied. The tetrasubstituted compound showed a redshift in absorption spectra and peri substitution broadened the absorption spectrum. Theoretical studies were in agreement with the photophysical and electrochemical studies. In the single-crystal analysis of compound 7, two molecules were packed in a head-to-tail motif by following the ABC packing pattern. These compounds were used in the fabrication of DSSCs, in which tetrasubstituted compound 10 gave the highest efficiency. This finding highlights the fact that more donor groups on a single acceptor unit may be better to enhance the power conversion efficiency of future dyes. A detailed investigation of regioselectivity in bromination of PMI and optimization of DSSC performance of the synthesized molecules are in progress in our laboratory.

Experimental Section

Materials: All chemicals and reagents were purchased from commercial suppliers (Sigma–Aldrich and Merck) and used without further purification. Solvents for spectroscopic measurements were spectral-grade quality. All reactions were monitored by TLC carried out on silica gel plates. Preparative separations were performed by column chromatography on silica gel grade 60 (0.040–0.063 mm) from Merck.

Instrumentation and characterization: ¹H NMR spectra were recorded on Bruker Avance AV300 (300 MHz) and AV500 (500 MHz) spectrometers. The peaks are represented as s=singlet, d=doublet, t=triplet, m=multiplet, and br = broad. The chemical shifts are reported in ppm and referenced to the residual solvent peak. MALDI-TOF mass spectra were obtained on a Bruker Autoflex III spectrometer. Elemental analysis was carried out on an Elementar Vario Micro Cube. UV/Vis and emission spectra were measured on a Shimadzu UV-1601 PC spectrophotometer and RF-5301PC Shimadzu spectrofluorophotometer. Current-voltage (I-V) characteristics under simulated AM 1.5 illumination were measured by using a Keighley Source Meter and the PVIV software package (Newport). Simulated AM 1.5 illumination was provided by a Newport class A solar simulator and light intensity was measured by using a calibrated Si reference cell. The thickness of nanocrystalline TiO₂ layers was determined by profilometry measurements made by means of an Alpha-Step IQ surface profiler.

Cyclic voltammograms were recorded with a computer-controlled CHI electrochemical analyzer at a constant scan rate of 100 mV s⁻¹. Measurements were performed in an electrolyte solution of 0.1 m tetrabutylammonium hexafluorophosphate dissolved in degassed dichloromethane. The electrochemical cell consisted of a three-electrode system with a platinum disk as the working electrode, a platinum rod as the counter electrode, and a standard calomel electrode (SCE) as the reference electrode. The potentials were calibrated by using ferrocene as the internal standard. The onsets of oxidation (E_{ox}^{onset}) and reduction (E_{rod}^{onset}) were used to calculate the HOMO and LUMO energy levels by using the relationships $E_{\rm HOMO} = -(4.8 + E_{rod}^{onset})$, respectively. Geometry optimizations were performed in Gaussian 00^[17] at the DFT level with the B3LYP functional and the 6-31G(d) basis set. The HOMO and LUMO surfaces were generated from the optimized geometries by using GaussView 5.^[18]

N-(2-Ethylhexyl)perylene-3,4-dicarboximide (1): Following the literature procedure,^[12] samples of perylene-3,4,9,10-tetracarboxylic acid anhydride (PDA; 2.5 g, 6.4 mmol), 2-ethylhexylamine (0.42 g, 3.3 mmol), Zn(OA-

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c)₂·2H₂O (0.39 g, 1.81 mmol), imidazole (13 g), and H₂O (6 mL) were placed in an autoclave. The mixture was heated at 190 °C. After 24 h, the reaction mixture was cooled to room temperature and poured into water (30 mL). The resulting mixture was vacuum filtered and washed with water (50 mL×4) and methanol (50 mL). The isolated solid was purified by flash column chromatography with chloroform as the eluent to give a red compound (m.p. > 300 °C, 24 %, 0.66 g). ¹H NMR (300 MHz, CDCl₃): $\delta = 8.06$ (d, J = 7.20 Hz, 2H), 7.85 (d, J = 7.80 Hz, 2H), 7.74 (d, J = 7.80 Hz, 2H), 7.80 (d, J = 7.80 (d, J = 7.80 Hz, 2H), 7.80 (d, J = 7.88.10 Hz, 2 H), 7.61 (d, J = 7.80 Hz, 2 H), 7.31 (t, $J_1 = J_2 = 7.80$ Hz, 2 H), 4.05-4.00 (m, 2H; N-CH₂), 1.94-1.90 (m, 1H), 1.44-1.34 (m, 8H), 0.99-0.89 ppm (m, 6H); 13 C NMR (75 MHz, CDCl₃): $\delta = 163.9$, 136.2, 133.8, 130.7, 130.4, 129.0, 128.5, 127.2, 126.5, 125.8, 123.0, 120.4, 119.5, 44.0, 38.1, 30.8, 28.8, 24.1, 23.2, 14.2, 10.7 ppm; FAB MS: m/z: 433.21 [M]+; elemental analysis calcd (%) for C₃₀H₂₇NO₂: C 83.11, H 6.28, N 3.23; found: C 83.21, H 6.34, N 3.17.

Bromination of N-(2-ethylhexyl)perylene-3,4-dicarboximide: N-(2-Ethylhexyl)perylene-3,4-dicarboxydiimide (0.500 g, 1.15 mmol) was dissolved in chloroform (30 mL) in a two-neck round-bottomed flask (100 mL), bromine (3 mL, 58 mmol) was added, and the solution was heated at reflux for 10 h. The reaction mixture was cooled to room temperature, excess bromine was removed by passing through an aqueous solution of sodium thiosulfate with an air pump, and solvent was removed on a rotary evaporator. The crude brominated PMI (0.80 g) showed two closely separated spots on a TLC plate by using an eluent of dichloromethane and hexane (1:1). The crude mixture (100 mg) was purified by silica gel column chromatography and the ¹H NMR spectrum of the spot with an $R_{\rm f}$ value of 0.78 (65 mg) showed two sets of peaks, which were assigned to 1,6,9,10-tetrabromoPMI (4) and 1,6,9-tribromoPMI (2) present in a ratio of approximately 1:4. The ¹H NMR spectrum of a second spot with an $R_{\rm f}$ value of 0.74 (0.26 mg) was assigned to 1,9,10-tribromoPMI (3). The molar ratio of compounds 2-4 was approximately 4:2:1, respectively.

N-(2-Ethylhexyl)-1,6,9,10-tetrabromoperylene-3,4-dicarboximide (4): Compound 4 was precipitated from a solution of the mixture of 2 and 4 in dichloromethane by using hexane, and the procedure was repeated five times to give a red precipitate (m.p. >300 °C) with a yield of 13 % (from ¹H NMR analysis). ¹H NMR (300 MHz, CDCl₃): $\delta = 8.92$ (d, J =8.40 Hz, 2H; Per-H), 8.84 (s, 2H; Per-H), 8.10 (d, J=8.40 Hz, 1H; Per-H), 4.14-4.10 (m, 2H; N-CH₂), 1.96-1.90 (m, 1H), 1.40-1.30 (m, 8H), 0.96-0.87 ppm (m, 6H); MALDI-TOF MS: m/z: 749.69 [M]+; elemental analysis calcd (%) for C₃₀H₂₃Br₄NO₂: C 48.10, H 3.09, Br 42.67, N 1.87; found: C 48.02, H 3.18, Br 42.69, N 1.95.

N-(2-Ethylhexyl)-1,6,9-tribromoperylene-3,4-dicarboximide (2): After repetitive precipitation of compound 4 from the mixture, a small amount of compound 2 was formed as a red compound (m.p. 217 $^{\circ}\mathrm{C})$ from the remaining solution with a yield of 54 %. ¹H NMR (500 MHz, CDCl₃): $\delta =$ 9.22 (d, J=7.00 Hz, 1 H; Per-H), 9.00 (d, J=8.20 Hz, 1 H; Per-H), 8.81 (s, 1H; Per-H), 8.79 (s, 1H; Per-H), 8.37 (d, J=8.20 Hz, 1H; Per-H), 7.91 (d, J = 8.20 Hz, 1H; Per-H), 7.30 (t, $J_1 = J_2 = 8.20$ Hz, 1H), 4.16–4.07 (m, 2H; N-CH₂), 1.93-1.91 (m, 1H), 1.41-1.30 (m, 8H), 0.96-0.88 ppm (m, 6H); ¹³C NMR (125 MHz, CDCl₃): $\delta = 162.7$, 138.0, 134.8, 134.6, 131.5, 130.7, 130.2, 129.7, 129.4, 128.7, 127.4, 126.8, 126.6, 126.3, 126.1, 120.9, 120.8, 119.1, 118.8, 44.4, 37.9, 30.7, 28.7, 24.1, 24.0, 14.1, 10.6 ppm; MALDI-TOF MS: m/z: 670.21 $[M]^+$; elemental analysis calcd (%) for $C_{30}H_{24}Br_{3}NO_{2}{:}\ C$ 53.76, H 3.61, Br 35.77, N 2.09; found: C 53.71, H 3.54, Br 35.67, N 2.06.

N-(2-Ethylhexyl)-1,9,10-tribromoperylene-3,4-dicarboximide (3): Compound 3 was orange-red in color (m.p. 170-172°C) with a yield of 27%. ¹H NMR (500 MHz, CDCl₃): $\delta = 9.05$ (d, J = 8.20 Hz, 1 H; Per-H), 8.85 (d, J=8.20 Hz, 1H; Per-H), 8.71 (s, 1H; Per-H), 8.49 (d, J=8.20 Hz, 1H; Per-H), 8.01 (d, J=9.45 Hz, 1H; Per-H), 7.84 (d, J=8.80 Hz, 1H; Per-H), 7.79 (d, J=8.20 Hz, 1H; Per-H), 4.16–4.08 (m, 2H; N-CH₂), 1.96–1.94 (m, 1 H), 1.41–1.32 (m, 8 H), 0.96–0.88 ppm (m, 6 H); ¹³C NMR $(125 \text{ MHz}, \text{ CDCl}_3): \delta = 163.4, 162.9, 137.7, 137.1, 135.1, 133.6, 131.2,$ 130.4, 129.8, 129.7, 129.6, 129.0, 128.6, 126.9, 126.8, 126.6, 125.4, 122.2, 121.2, 120.9, 117.8, 44.3, 38.0, 30.7, 28.7, 24.1, 23.1, 14.1, 10.6 ppm; MALDI-TOF MS: m/z: 670.11 [M]⁺; elemental analysis calcd (%) for C30H24Br3NO2: C 53.76, H 3.61, Br 35.77, N 2.09; found: C 53.73, H 3.58, Br 35.69, N 2.05.

Synthesis of TPA-substituted PMI molecules by Suzuki coupling reaction: The brominated mixture of PMI (0.336 g) and 4-(diphenylamino)phenylboronic acid (0.578 g, 2 mmol) was dissolved in THF (20 mL) in a two-neck round-bottomed flask (100 mL) under a nitrogen atmosphere. A nitrogen-purged aqueous solution of 1 M K₂CO₃ (10 mL) was added to this reaction mixture. Catalyst [Pd(PPh₃)₄] (0.058 g, 0.05 mmol) was added and the mixture was stirred for 24 h at 80 °C under a nitrogen atmosphere. The reaction mixture was allowed to cool to room temperature and was extracted with dichloromethane. The collected organic layer was dried over anhydrous sodium sulfate and filtered. The excess solvent was removed under reduced pressure. The crude mixture showed three spots on TLC plates with 5% ethyl acetate in hexane as the eluent, with $R_{\rm f}$ values of 0.39, 0.35, and 0.32. The crude mixture was purified by column chromatography by using 5% ethyl acetate in hexane as the mobile phase and all three compounds were collected. The mole ratio of compounds 5-7 was 4:2:1, respectively, which was also comparable to the brominated crude mixture.

N-(2-Ethylhexyl)-1,6,9-tri(triphenylamine)perylene-3,4-dicarboximide (5): Compound 5 ($R_{\rm f} = 0.39$) was obtained as a dark blue solid (290 mg, m.p. 146–148°C). ¹H NMR (300 MHz, CDCl₃): $\delta = 8.56$ (s, 2H; Per-H), 7.96 (d, J=8.07 Hz, 1H; Per-H), 7.88 (m, 2H; Per-H), 7.38-7.34 (m, 3H), 7.32-7.27 (m, 13 H), 7.20-7.14 (m, 22 H), 7.09-7.02 (m, 6 H), 4.19-4.11 (m, 2H; N-CH₂), 1.98 (m, 1H), 1.43-1.32 (m, 8H), 0.97-0.87 ppm (m, 6H); $^{13}\text{C}\,\text{NMR}$ (75 MHz, CDCl₃): $\delta\!=\!164.4,\;147.6,\;147.51,\;147.49,\;147.36,$ 147.31, 141.6, 138.8, 138.6, 137.6, 137.5, 135.6, 135.3, 135.2, 133.3, 131.5, 130.9, 130.7, 130.5, 130.2, 130.1, 130.0, 129.4, 129.3, 128.8, 128.0, 127.7, 127.1, 126.3, 125.0, 124.7, 124.6, 124.5, 124.4, 123.3, 123.1, 123.0, 122.9, 120.0, 119.8, 44.0, 38.0, 30.8, 28.8, 24.1, 23.1, 14.1, 10.7 ppm; MALDI-TOF MS: m/z: 1163.74 $[M]^+$; elemental analysis calcd (%) for C84H66N4O2: C 86.72, H 5.72, N 4.82; found: C 86.64, H 5.66, N 4.78.

N-(2-Ethylhexyl)-1,9,10-tri(triphenylamine)perylene-3,4-dicarboximide

(6): Compound 6 ($R_f = 0.35$) was obtained as a black solid (140 mg, m.p. 156–158 °C). ¹H NMR (300 MHz, CDCl₃, ppm): $\delta = 8.59$ (s, 1H; Per-H), 8.17 (d, J=8.22 Hz, 1 H; Per-H), 8.10 (d, J=8.73 Hz, 1 H; Per-H), 7.93 (d, J = 7.89 Hz, 1H; Per-H), 7.76 (d, J = 8.22 Hz, 1H; Per-H), 7.53 (d, J =8.88 Hz, 1H; Per-H), 7.45-7.40 (m, 3H), 7.37-7.29 (m, 15H), 7.21-7.10 (m, 15H), 7.08-7.03 (m, 10H), 4.17-4.12 (m, 2H; N-CH₂), 1.97 (m, 1H), 1.42–1.32 (m, 8H), 0.97–0.87 ppm (m, 6H); 13 C NMR (75 MHz, CDCl₃): $\delta\!=\!164.50,\;164.46,\;147.8,\;147.6,\;147.5,\;147.4,\;147.3,\;141.5,\;141.0,\;140.7,$ 137.6, 137.4, 137.0, 136.7, 136.7, 136.6, 135.4, 135.2, 135.0, 133.3, 133.2, 131.1, 131.0, 130.9, 130.7, 130.6, 130.2, 130.1, 129.9, 129.43, 129.40, 129.3, 129.2, 129.1, 128.4, 128.2, 127.9, 127.2, 126.4, 125.1, 124.9, 124.8, 124.7, 124.6, 124.5, 124.4, 124.0, 123.9, 123.4, 123.3, 123.2, 123.1, 122.9, 122.8, 119.8, 119.5, 44.1, 38.0, 30.8, 28.8, 24.0, 23.1, 14.1, 10.7 ppm; MALDI-TOF MS: m/z: 1163.70 [M]⁺; elemental analysis calcd (%) for $C_{84}H_{66}N_4O_2{:}\ C$ 86.72, H 5.72, N 4.82; found: C 86.67, H 5.69, N 4.88.

N-(2-Ethylhexyl)-1,6,9,10-tetra(triphenylamine)perylene-3,4-dicarbox-

imide (7): Compound 7 ($R_f = 0.32$) was obtained as a dark-blue solid (80 mg, m.p. 169 °C). ¹H NMR (300 MHz, CDCl₃, ppm): $\delta = 8.58$ (s, 2H; Per-H), 7.90 (d, J=7.90 Hz, 2H; Per-H), 7.37-7.32 (m, 6H), 7.29-7.27 (m, 8H), 7.23-7.13 (m, 30H), 7.07-7.03 (m, 8H), 6.92 (d, J=8.55 Hz, 4H), 6.83 (d, J=8.55 Hz, 4H), 4.20-4.15 (m, 2H; N-CH₂), 2.04-1.99 (m, 1H), 1.44–1.33 (m, 8H), 0.98–0.88 ppm (m, 6H); ¹³C NMR (75 MHz, $CDCl_3$): $\delta = 164.5, 147.5, 147.4, 147.3, 146.3, 142.3, 138.3, 137.6, 136.0,$ 135.6, 135.3, 133.0, 130.6, 130.1, 130.0, 129.9, 129.8, 129.3, 129.0, 127.7, 127.1, 125.1, 124.6, 124.5, 123.2, 123.1, 120.8, 119.7, 44.1, 38.0, 30.8, 28.8, 24.1, 23.1, 14.1, 10.7 ppm; MALDI-TOF MS: m/z: 1406.82 [M]+; elemental analysis calcd (%) for $C_{102}H_{79}N_5O_2$: C 87.09, H 5.66, N 4.98; found: C 87.13, H 5.60, N 5.01.

General procedure to synthesize PMAs: TPA-substituted PMI (0.10 mmol) and KOH (560 mg, 10.0 mmol) were added to a solution of tert-butyl alcohol (15 mL) and heated to reflux. After stirring for 2 h, the reaction mixture was poured into a mixture of acetic acid (20 mL) and 1 N HCl (20 mL) and stirred for 5 h at room temperature. The resulting mixture was poured into a biphasic mixture of dichloromethane (100 mL) and H₂O (50 mL). After separation, the organic layer was washed with brine (100 mL) and dried over MgSO₄. After filtration and

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evaporation of the solvent, the residue was subjected to silica gel column chromatography by using hexane/dichloromethane (1:3).

N-(2-Ethylhexyl)(1,6,9-triphenylamine)perylene-3,4-dicarboxylic acid anhydride (8): Compound 8 was obtained as a black solid (72 mg, 69%, m.p. 177°C). ¹H NMR (300 MHz, CDCl₃): δ =8.53 (s, 2H; Per-H), 8.00 (d, *J*=8.40 Hz, 2H; Per-H), 7.92–7.88 (m, 2H), 7.37–7.34 (m, 2H), 7.33–7.27 (m, 12H), 7.24–7.04 ppm (m, 30H); ¹³C NMR (75 MHz, CDCl₃): δ = 160.92, 147.8, 147.7, 147.6, 147.45, 147.40, 142.5, 139.1, 138.9, 137.4, 137.2, 137.0, 136.6, 136.5, 132.9, 131.5, 131.1, 131.0, 130.9, 130.7, 130.4, 129.8, 129.4, 128.9, 128.3, 127.2, 126.4, 125.1, 124.8, 124.7, 124.6, 124.34, 124.3, 123.6, 123.4, 123.3, 122.7, 115.7, ppm; MALDI-TOF MS: *m*/*z*: 1052.55 [*M*]⁺; elemental analysis calcd (%) for C₇₆H₄₉N₃O₃: C 86.75, H 4.69, N 3.99; found: C 86.67, H 4.66, N 4.08.

N-(2-Ethylhexyl)(1,9,10-triphenylamine)perylene-3,4-dicarboxylic acid anhydride (9): Compound 9 was obtained as a black solid (63 mg, 60%, m.p. 203 °C). ¹H NMR (300 MHz, CDCl₃): $\delta = 8.47$ (s, 1H; Per-H), 8.11 (d, J = 8.70 Hz, 1 H; Per-H), 8.01 (d, J = 8.22 Hz, 1 H; Per-H), 7.88 (d, J =8.07 Hz, 1H; Per-H), 7.63 (d, J = 8.22 Hz, 1H; Per-H), 7.53 (d, J =9.06 Hz, 1H; Per-H), 7.39 (d, J=8.55 Hz, 1H; Per-H), 7.36-7.28 (m, 16H), 7.25–7.00 ppm (m, 26H); 13 C NMR (75 MHz, CDCl₃): $\delta = 161.0$, 160.8, 148.1, 147.9, 147.84, 147.80, 147.4, 147.3, 147.2, 142.8, 142.5, 142.0, 141.7, 139.3, 139.1, 137.9, 137.6, 137.1, 136.9, 136.7, 136.1, 136.0, 135.9, 135.8, 132.8, 132.7, 132.2, 131.4, 131.2, 131.0, 130.9, 130.74, 130.70, 130.3, 130.1, 130.0, 129.9, 129.5, 129.4, 129.3, 129.1, 128.9, 128.8, 128.3, 127.9, 127.6, 126.5, 125.2, 125.0, 124.9, 124.8, 124.7, 124.6, 124.1, 123.7, 123.6, 123.5, 123.4, 123.3, 122.8, 122.6, 115.6, 115.4, 114.9, 114.7 ppm; MALDI-TOF MS: m/z: 1052.54 [M]⁺; elemental analysis calcd (%) for C₇₆H₄₉N₃O₃: C 86.75, H 4.69, N 3.99; found: C 86.77, H 4.61, N 4.02.

N-(2-Ethylhexyl)-1,6,9,10-tetra(triphenylamine)perylene-3,4-dicarboxylic acid anhydride (10): Compound 10 was obtained as a dark-blue solid (87 mg, 67%, m.p. 197°C). ¹H NMR (300 MHz, CDCl₃): δ =8.55 (s, 2H; Per-H), 7.93 (d, *J*=8.10 Hz, 2H; Per-H), 7.34–7.27 (m, 12H), 7.24–7.13 (m, 30 H), 7.09–7.02 (m, 8H), 6.92 (d, *J*=8.70 Hz, 4H), 6.83 ppm (d, *J*=8.70 Hz, 4H); ¹³C NMR (75 MHz, CDCl₃): δ =161.0, 147.6, 147.4, 147.3, 146.5, 143.4, 138.6, 137.4, 137.0, 136.7, 135.6, 133.5, 130.6, 130.5, 130.0, 129.9, 129.6, 129.4, 129.3, 129.0, 127.2, 125.2, 124.9, 124.6, 124.4, 123.4, 123.3, 120.7, 115.3 ppm; MALDI-TOF MS: *m*/*z*: 1295.65 [*M*]⁺; elemental analysis calcd (%) for C₉₄H₆₂N₄O₃: C 87.15, H 4.82, N 4.32; found: C 87.17, H 4.86, N 4.28.

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FULL PAPER



Multiple donors: The design and synthesis of a series of triphenylamine (TPA)-functionalized perylene monoanhydrides from multibrominated perylene monoimides (PMIs) is reported (see figure). The number and position

of TPA groups and conformation of the PMI molecules influence the photophysical and electrochemical properties of the compounds. The tetrasubstituted derivative gives the highest efficiency in dye-sensitized solar cells.

Perylene Dyes -

A. Keerthi, Y. Liu, Q. Wang, S. Valiyaveettil*.....

Synthesis of Perylene Dyes with **Multiple Triphenylamine Substituents**

