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Self-Organization of Phthalocyanine−[60]Fullerene Dyads in Liquid Crystals

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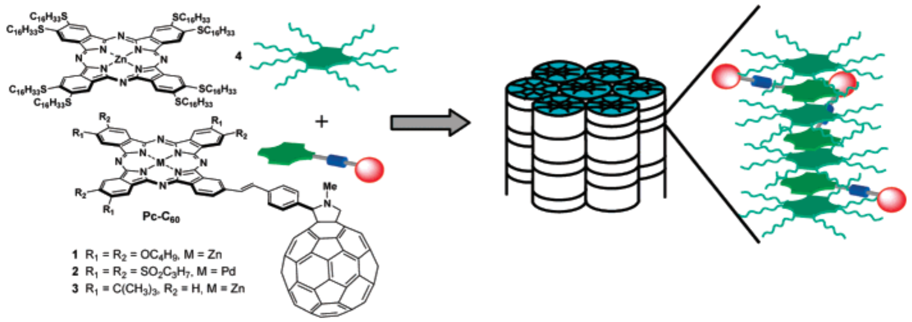

The use of blends in which a mesogen induces mesomorphism into a non-mesogenic compound has made possible the self-organization of phthalocyanine−[60]fullerene (Pc-C_{60}) dyads into liquid crystals. Pc-C_{60} dyads **1**, **2**, or **3**, in which two photoactive units are brought together by a phenylenevinylene spacer, have been synthesized through a Heck reaction that links 4-vinylbenzaldehyde to a monoiodophthalocyanine precursor, followed by standard cycloaddition of azomethine ylides−generated from the formylPc derivative and *N*-methylglycine−to one of the double bonds of C_{60}. The mesomorphic and thermal properties of different mixtures formed by the liquid-crystalline phthalocyanine **4** and dyads **1**, **2**, or **3** were examined using polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). DSC diagrams of the blends show clear transitions from the crystalline state to a mesophase, and the measured structural parameters obtained from the powder diffraction experiments are consistent with a discotic hexagonal columnar (Col_h) structure. Considering that segregation in domains of separated molecules of Pc-C_{60} dyad and phthalocyanine **4** would preclude mesomorphism due to the mismatch in the column diameter and to the lack of mesogenic character of the pure dyads, a predominance of alternating stacking is proposed. Additionally, the observed decrease in the calculated density of the blend mesophases relative to the mesophase of pure compound **4** is important evidence in this direction.

Introduction

Phthalocyanines (Pcs), one of the best known synthetic porphyrin analogues, have been considered for many years fashionable building blocks to construct functional materials for technological applications.[1] More recently, donor−acceptor dyads formed by phthalocyanine and fullerene moieties have attracted growing attention,[2] since these photoactive systems can give rise to long-lived photoinduced charge-separated states,[3] opening the way to devices capable of performing complex functions such as molecular switches, receptors, or photovoltaic cells.

It has been shown that the efficiency of organic photovoltaics can be improved by controlling the supramolecular organization of the molecules at the nanometric scale.[4] Self-organization in liquid-crystalline phases offers a unique route to the formation of columnar stacks of photoactive molecules.[5] There are already

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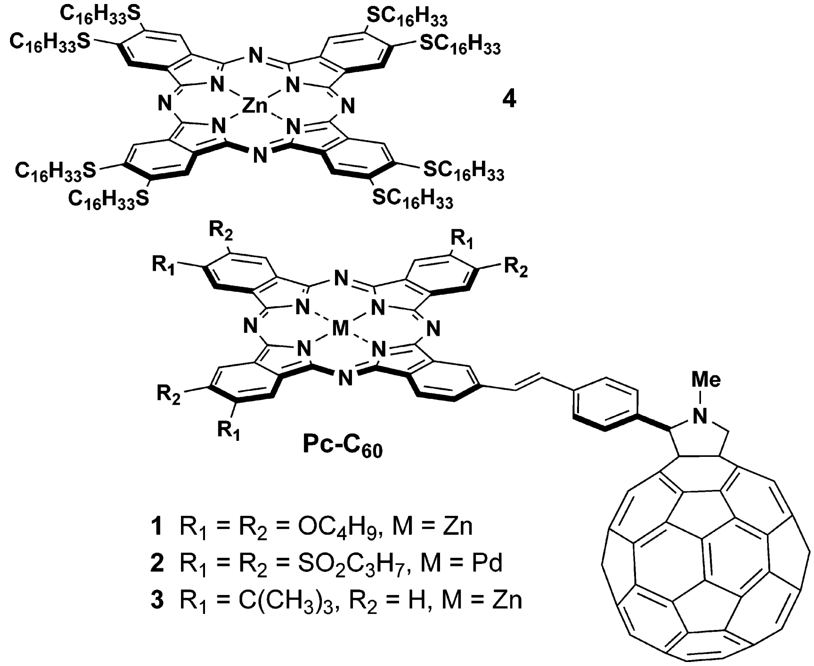

4

Pc-C$_{60}$

1 R$_1$ = R$_2$ = OC_4H_9, M = Zn
2 R$_1$ = R$_2$ = $SO_2C_3H_7$, M = Pd
3 R$_1$ = $C(CH_3)_3$, R$_2$ = H, M = Zn

FIGURE 1. Components for the liquid-crystalline phthalocyanine−C$_{60}$ blends.

in the literature many examples of liquid crystals formed by either phthalocyanine[6] or fullerene[7] derivatives. However, to the best of our knowledge, mesogenic Pc-C$_{60}$ dyads have never been reported, most probably due to the tedious purification of the unsymmetrically substituted phthalocyanines when they possess long hydrocarbon chains at the periphery, which is a structural requirement to induce mesomorphism on this class of discotic molecules. Moreover, a bulky unit such as C$_{60}$ cannot be easily accommodated into a LC columnar organization.

The use of blends, in which a mesogen induces mesomorphism to a non-mesogenic compound, represents an elegant strategy to overcome this problem.[8] Herein, we describe for the first time the organization of Pc-C$_{60}$ dyads within liquid-crystalline phases. In this study, a hexagonal columnar phase was obtained by simply blending either compounds **1**, **2**, or **3**, bearing at the periphery butoxy, propylsulfonyl, and *tert*-butyl substituents, respectively, with the discotic mesogen Zn(II)-octakis(hexadecylthio)phthalocyanine (**4**) (Figure 1). Different types of substituents (electron donor butoxy, electron deficient propylsulfonyl, bulky *tert*-butyl groups) have been introduced at the periphery of the Pc moiety of the dyad to establish their influence in the final organization within the blend. Although

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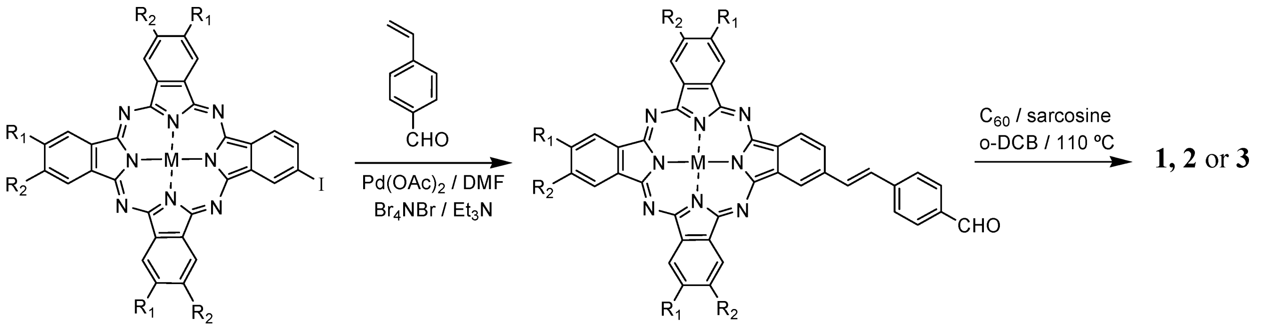
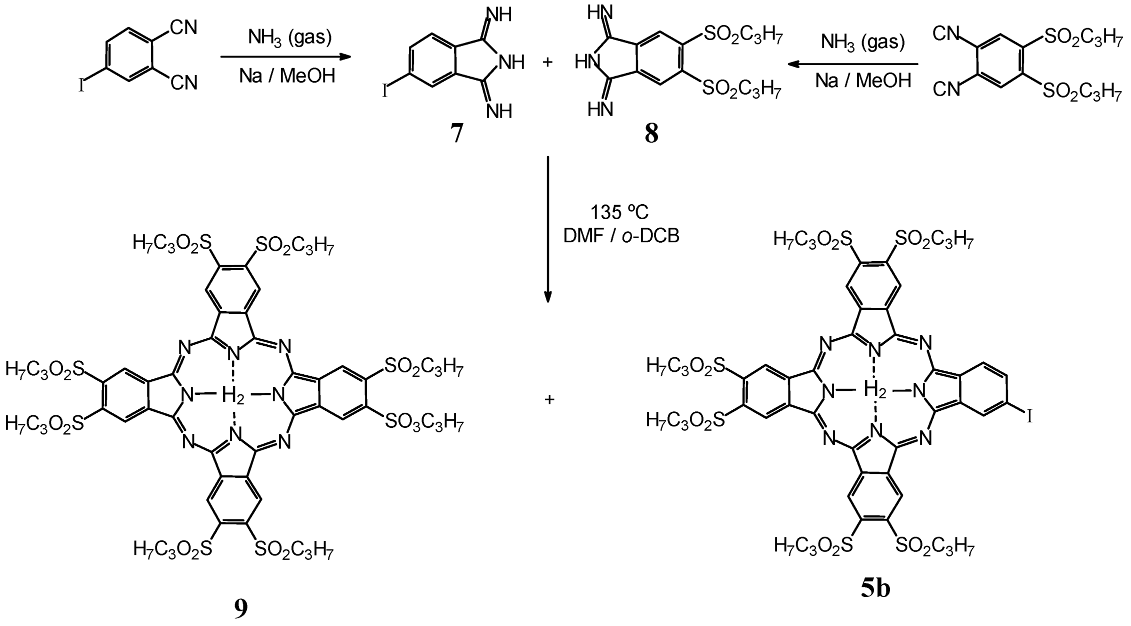
SCHEME 1. Synthesis of Pc-C_{60} Dyads 1, 2, and 3



5a $R_1 = R_2 = OC_4H_9$, M = Zn
5b $R_1 = R_2 = SO_2C_3H_7$, M = H_2
5c $R_1 = C(CH_3)_3$, R_2 = H, M = Zn

6a $R_1 = R_2 = OC_4H_9$, M = Zn (73%)
6b $R_1 = R_2 = SO_2C_3H_7$, M = Pd (47%)
6c $R_1 = C(CH_3)_3$, R_2 = H, M = Zn (61%)

SCHEME 2. Synthesis of Propylsulfonyl-Substituted Phthalocyanines 5b and 9



the self-organization of a non-mesogenic fullerene derivative into columnar liquid crystals has already been described following a similar strategy,[9] the well-known photoinduced charge-transfer properties of Pc-C_{60} dyads make the current approach potentially more suitable for the construction of new efficient phthalocyanine-based photovoltaic devices.

Results and Discussion

Synthesis. The synthesis of Pc-C_{60} dyads **1**,[3g] **2**, and **3** was carried out in two steps (Scheme 1). First, iodophthalocyanine precursors **5a**−**c**, bearing butoxy,[10] propylsulfonyl, and *tert*-butyl substituents,[11] respectively, were connected to 4-vinylbenzaldehyde[12] by means of a Heck reaction. Subsequent Prato reaction of the resulting Pc-formyl derivatives **6a**−**c** with C_{60} and sarcosine led to the target dyads.

In the case of the propylsulfonyl-substituted derivatives, the required Pd(II)-iodophthalocyanine precursor **5** was not described in the literature. Attempts to prepare it by cross condensation of the corresponding phthalonitriles in the presence of $Pd(OAc)_2$ led to the compound in very low yields. This result is not due to a lower reactivity of the 3,4-bis(propylsulfonyl)-phthalonitrile but to the necessary change of the solvent used in the macrocyclization to avoid nucleophilic displacement of the sulfonyl groups. Instead, an alternative route was employed in which 1,3-diiminoisoindolines **7**[13] and **8** were reacted in a refluxing mixture of DMF and *o*-DCB, leading to the formation of a statistical mixture of metal-free Pcs, from which phthalocyanines **5b** and **9** were separated by column chromatography (Scheme 2). For the Heck reaction of **5b** with 4-vinylbenzaldehyde, 1.1 equiv of $Pd(OAc)_2$ was used to accomplish in the same step both the C−C coupling and the introduction of the Pd atom into the central cavity of the macrocycle. The synthesis of the free-base formylPc **6b** was also attempted employing

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TABLE 1. Phase Transition Temperatures and Enthalpies for Compound 4 and Blends 4/1, 4/2, and 4/3 Determined by Differential Scanning Calorimetry[a]

sample	Cr	T [°C] (ΔH [J/g]) 1st scan	T [°C] (ΔH [J/g]) 2nd scan	Col$_h$	T [°C] (ΔH [J/g])	I
4	•	89 (35)	34 (54)	•	260 (4.3)	•
4/1	•	61 (13)	24 (17)	•	>250[b]	•
4/2	•	70 (15)	26 (11)	•	>250[b]	•
4/3	−	−	−	•	>250[b]	•

[a] Key: (•) phase is observed; (−) phase is not observed. Cr = crystalline phase. Col$_h$ = hexagonal columnar. I = isotropic liquid phase. [b] Transition observed only by POM.

lower amounts of the catalyst without success. Another important reaction parameter to be controlled was the temperature, since some extent of deiodination and homocoupling competitive processes from the starting iodoPc have been detected over 80 °C.

(Alkylsulfonyl)Pc derivatives are very rare in the literature despite their interesting properties. For instance, they are unique examples of soluble electron-acceptor phthalocyanines with a low tendency toward aggregation. Both iodoPc **5b** and the formylPc **6b** are intermediate compounds in the synthesis of dyad **2**, but also interesting derivatives in general for the organic chemists working on phthalocyanine synthesis.

The mesogenic phthalocyanine **4** was synthesized with a 49% yield by a standard macrocyclation procedure of 4,5-bis(hexadecylthio)phthalonitrile[14] in the presence of $ZnCl_2$ and DMAE as solvent.

All the compounds were fully characterized by NMR, FTIR, MALDI-MS, and UV/vis spectroscopy. The ^1H NMR spectra in $CDCl_3$ of dyads **2** and **3** are poorly resolved due to aggregation at the experimental NMR concentrations. However, signals assigned to the pyrrolidine ring can be clearly observed between 4.3 and 5.2 ppm, as well as the $N-CH_3$ resonance at 2.95 ppm. Concerning mass spectrometry, peaks corresponding to the $[M - C_{60}]^+$ fragment appear in the MALDI-TOF spectra of dyads, together with the molecular ions $[M^+]$ or $[M + H]^+$ as major species. Split Q-bands are observed in the UV/vis spectra in $CHCl_3$ of dyad **2** and its precursors. In both cases (dyads **2** and **3**) the Q-bands are shifted to higher wavelengths when compared to the spectra of the monoiodo precursors, as a consequence of the extended π-conjugation (all the spectra are shown in the Supporting Information).

Study of the Liquid-Crystalline Properties. The mesomorphic and thermal properties of each of the pure components, i.e., phthalocyanine **4** and the Pc-C_{60} dyads **1**, **2**, and **3**, were examined before blending, using polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). Compound **4** shows, as previously described for analogous phthalocyanines,[15] a hexagonal columnar (Col$_h$) mesophase between 89 and 260 °C (first heating cycle) or between 43 and 260 °C (second heating cycle). In contrast, the dyads **1**, **2**, and **3** do not present mesomorphic behavior but are crystalline and do not melt below 350 °C. Once the pure components were studied, 1:1 mixtures of phthalocyanine **4** and the dyads **1**, **2**, or **3** were prepared by evaporation of the solvent from THF solutions, and their phase behavior evaluated. Table 1 lists the phase transition temperatures and enthalpy changes established by DSC and POM experiments. In optical microscopy, all blends showed birefringence in a wide range up to 250 °C, although characteristic textures were not observed. The mesophases of the blends were found to be very viscous at low temperatures, and fluidity appeared only when the samples were heated well above 100 °C. As a consequence of this, not every DSC peak could be confirmed optically.

TABLE 2. X-ray Measurements on the Liquid-Crystalline Phases of Compound 4 and (1:1) Blends of 4/1, 4/2 and 4/3[a]

sample	T (°C)	M	d_{meas} (Å)	d_{calcd} (Å)	hkl	lattice constant a (Å)	calcd density (g·cm^{-3})
4	110	Col$_h$	30.8	31.0	100	35.8	1.12
			18.2	17.9	110		
			15.4	15.5	200		
			4.6 (br)				
			3.5				
4/1	110	Col$_h$	30.8	30.8	100	35.6	0.99
			4.6 (br)				
			3.45				
4/2	90	Col$_h$	32.8	32.7	100	37.8	0.91
			19.1	18.9	110		
			16.1	16.4	200		
			4.6 (br)				
			3.5				
4/3	25	Col$_h$	30.8	30.7	100	35.4	0.96
			17.6	17.7	110		
			15.3	15.3	200		
			4.6 (br)				
			3.4				

[a] Col$_h$: hexagonal columnar mesophase. d_{meas} and d_{calc} are the measured and calculated diffraction spacing. Br = broad. *hkl* are the indexations of the reflections corresponding to the Col$_h$ phase. *a* is the lattice parameter of the hexagonal columnar phase. For the calculation of *a* see the Supporting Information.

DSC diagrams of blends **4**/**1** and **4**/**2** show unequivocal transitions from the crystalline state to a mesophase (Supporting Information). Interestingly, the crystal−mesophase transition temperatures of the blends are slightly lower than that of the pure intrinsically mesogenic compound **4**. For instance, while **4** enters the liquid-crystalline phase at 89 °C, the heating curves for blends **4**/**1** and **4**/**2** show melting peaks at 61 and 70 °C, respectively. Repetitive heating and cooling scans result in a decrease of these transition temperatures and therefore in a broadening of the mesophase range. Concerning blend **4**/**3**, its DSC curves resemble the ones described above but are more poorly resolved, probably due to the bulkiness of the *tert*-butyl groups in dyad **3**, and it is not possible to clearly identify the transition peaks. The DSC curves are consistent with blend **4/3** being mesomorphic at room temperature, which was confirmed by XRD (see below).

The transition of the blends from the mesophase to the isotropic liquid was detected in all cases by optical microscopy. Although it is difficult to determine the temperature at which the transition occurs because it is slow and because of the absence of DSC peaks, we conclude that the mesophases are stable at least up to 250 °C (temperature close to the clearing point of pure **4**).

XRD studies were performed to identify the type of mesophase structure displayed by the mixed systems **4**/**1**, **4**/**2**, and **4**/**3** (X-ray diffractograms included in the Supporting Information). Table 2 summarizes the lattice parameters obtained from these experiments, carried out at temperatures close to 100 °C, except for blend **4/3**, which is liquid cystalline at room temperature.

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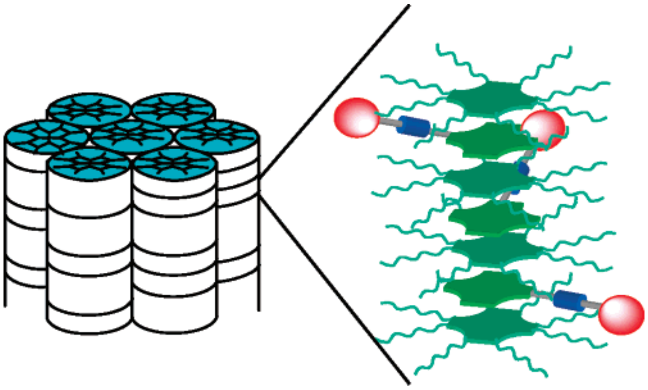

FIGURE 2. Schematic representation of the most probable structure of the mesophases formed by the Pc/Pc-C_{60} blends **4**/**1**, **4**/**2**, and **4**/**3**.

Powder diffraction patterns of all samples contain the typical reflections of a columnar mesophase of substituted phthalocyanines. In the low-angle region, a set of up to three reflections corresponding to a reciprocal spacing ratio of $1{:}3^{1/2}{:}2$, consistent with a two-dimensional hexagonal lattice, is present. Hence, a discotic hexagonal columnar (Col_h) structure of the mesophases can be proposed. The hexagonal lattice constant *a* can be deduced from these spacing values.

In the high-angle region of the X-ray patterns there are two diffuse scattering haloes: the first, very broad and typically observed in liquid-crystalline phases, corresponds to an average distance of 4.6 Å and arises from short-range interactions between the conformationally disordered aliphatic chains; the second is not so broad and corresponds to a distance of 3.4−3.5 Å, characteristic of the stacking of the disc-like molecules.

In all cases, the measured structural parameters are consistent with a discotic hexagonal columnar (Col_h) structure, and the decrease in the calculated density of the blend mesophases relative to the pure mesophase of compound **4** (Table 2) suggest an alternating stacking. However, considering that the order arising from the fullerene moieties is not visible in the powder diffractograms, the existence of some disorder cannot be excluded from these results (i.e., the alternating stacking is probably not long range). We actually propose a mixed model as the most probable one to explain the mesophase structure, with a predominance of alternating stacks of dyad and phthalocyanine **4** and some domains with randomly distributed Pc-C_{60} molecules. Figure 2 schematically depicts a hypothetical representation of the proposed alternating stacks. The predominance of alternating stacking is evident considering that segregation in domains of separated molecules of dyad and phthalocyanine **4** would preclude mesomorphism due to the mismatch in the column diameter and to the lack of mesogenic character of the pure dyads.

Conclusions

In conclusion, induced mesomorphism by blending a non-mesogenic molecule with a mesogen one represents a new strategy to organize phthalocyanine-C_{60} dyads into liquid crystals. In particular, the discotic phthalocyanine **4** was mixed with different non-mesogenic Pc-C_{60} dyads (namely, **1**, **2**, or **3**). In all cases, a hexagonal columnar mesophase was observed whatever the peripheral substituent on the phthalocyanine unit. We envisage that the same approach described in this paper could be used to organize at a supramolecular level other non-mesogenic dyads in which the phthalocyanine is linked to another photo- or electroactive subunit. Since phthalocyanine-based dyads, including the Pc-C_{60} dyad **1**,[3g] can undergo photoinduced electron transfer in appropriate conditions, the current approach could be also potentially useful in the photovoltaics field for improving the morphology in bulk heterojunctions by increasing the dissociation efficiency of bound electron−hole pairs at the donor−acceptor interface. Future experiments will be devoted to explore the photovoltaic properties of these kinds of systems.

Experimental Section

Pc-C_{60} Dyad 2. A mixture of C_{60} (40 mg, 0.055 mmol) and sarcosine (1.6 mg, 0.018 mmol) was dissolved in 6 mL of *o*-DCB under argon atmosphere at 60 °C. Afterward, a solution of phthalocyanine **6b** (25 mg, 0.018 mmol) in 4 mL of *o*-DCB was added. The reaction mixture was heated at 110 °C for an additional 8 h. After being cooled to room temperature the solvent was evaporated. The crude was purified by column chromatography on silica gel. Nonreacted C_{60} was eluted with toluene, while a mixture of toluene/THF (20:1) was used to elute compound **2**. Finally, the product was triturated with methanol and washed with acetone and ethyl acetate, obtaining 15 mg of a dark blue solid. Yield: 40%. Mp >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.0−9.5 (m, 6H), 9.2−8.8 (m, 2H), 8.2 (m, 1H), 7.9 (m, 4H), 7.7, 7.3 (AB system, 2H), 5,12 (s, 1H), 5.1 (d, $J = 9.38$ Hz, 1H), 4.37 (d, $J = 9.38$ Hz, 1H), 4.1 (m, 12H), 2.95 (s, 3H), 2.2 (m, 12H), 1.2 ppm (m, 18H). FT-IR (KBr) ν 3443 (ArC−H), 2962, 2922, 2852 (CH), 1637 (C═C), 1508, 1458 (C−N), 1292, 1145, 1082 (SO_2), 1030, 921, 875 cm^{-1}. UV/vis ($CHCl_3$) λ_{max} (log ϵ) 698 (4.98), 665 (5.08), 644 (4.77), 605 (4.56), 432 (4.05), 342 (5.02), 257 nm (5.21). MALDI-TOF MS (dithranol) *m/z* 2130 $[M + H]^+$, 2129 $[M^+]$, 1408 $[M - C_{60}]^+$. Anal. Calcd for $C_{121}H_{62}N_9O_{12}PdS_6$ (2132.65): C, 68.15; H, 2.93; N, 5.91; S, 9.02. Found: C, 68.03; H, 3.01; N, 5.87; S, 8.98.

Pc-C_{60} Dyad 3. A mixture of C_{60} (96 mg, 0.13 mmol) and sarcosine (4 mg, 0.045 mmol) was dissolved in 10 mL of *o*-DCB under argon atmosphere at 60 °C. Afterward, a solution of phthalocyanine **6c** (39 mg, 0.045 mmol) in 5 mL of *o*-DCB was added. The reaction mixture was heated at 110 °C for an additional 8 h. After being cooled to room temperature the solvent was evaporated. The crude was purified by column chromatography on silica gel. Nonreacted C_{60} was eluted with toluene, while a mixture of toluene/THF (50:1) was used to elute compound **3**. Further purification by a Bio-Beads column in THF was carried out to remove bisaduct derivatives. Finally, the product was triturated with methanol and washed with acetone and ethyl acetate, obtaining 28 mg of a dark green solid. Yield: 39%. Mp >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.6 (m, 9H), 7.9 (m, 3H), 7.7 (m, 4H), 7.7, 7.4 (AB system, 2H), 5.06 (s, 1H), 5.05 (d, $J = 8.8$ Hz, 1H), 4.34 (d, $J = 8.8$ Hz, 1H), 2.95 (s, 3H), 1.7 ppm (m, 27H). FT-IR (KBr) ν 3442 (ArC−H), 2952, 2778, (CH), 1611 (C═C), 1487 (C−N), 1089, 747, 527 cm^{-1}. UV/vis ($CHCl_3$) λ_{max} (log ϵ) 692 (5.19), 621 (4.48), 435 (4.32), 347 (5.04), 256 nm (5.20). HR-MALDI-TOF MS (dithranol) *m/z* ($C_{115}H_{51}N_9Zn$) calcd 1621.3556, found 1621.3552. Anal. Calcd for $C_{115}H_{51}N_9Zn{\cdot}H_2O$ (1642.101): C, 84,11; H, 3.25; N, 7.68. Found: C, 84.25; H, 3.29; N, 7.40.

Mesogenic Phthalocyanine 4. A mixture of 4,5-bis(hexadecylthio)phthalonitrile[12] (300 mg, 0.47 mmol), $ZnCl_2$ (16 mg, 0.12 mmol), and DBU (0.07 mL, 0.47 mmol) in DMAE (5 mL) was refluxed under argon for 16 h. The reaction mixture was cooled and separated by filtration. The remaining precipitate was washed with methanol. The residue was purified by column chromatography (silica gel, $CHCl_3$/hexane 9:1) and triturated with ethyl acetate to afford 188 mg of **4** as a dark green solid. Yield: 61%. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.29 (br s, 8H), 3.1 (m, 16H), 1.8 (m, 16H), 1.4−1.0 (m, 208H), 0.84 ppm (t, $J = 7.0$ Hz, 24H). MS-LSIMS (3-NOBA) *m/z* 393 $[M + H^+]$. FT-IR (KBr) ν 3074, 2930, 2855

(C−H), 1480, 1390, 1350, 1275, 1080, 975, 750 cm^{-1} (S−CH$_2$). UV/vis (CHCl$_3$) λ_{max} (log ϵ) 711 (5.36), 640 (4.57), 368 (4.84), 330 nm (4.75). MALDI-TOF MS (dithranol) *m/z* 2625.8 [M$^+$].

Iodophthalocyanine 5b. A DMF/*o*-DCB (1:1, 5 mL) solution of 1,3-diiminoisoindolines **7**[13] (60 mg, 0.22 mmol) and **8** (316 mg, 0.89 mmol) was heated at 140 °C under argon atmosphere for 12 h. After being cooled to room temperature, the solvent was removed under reduced pressure and the crude was triturated with methanol/water (3:1). The resulting dark blue solid was then purified by column chromatography on silica gel, using CHCl$_3$/THF (40:1) as eluent. The symmetrically substituted phthalocyanine was first eluted followed by the monoiodo derivative **5b**. Yield: 35%. Mp >250 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.40 (s, 2H), 10.02 (s, 1H), 9.99 (s, 1H), 9.78 (s, 1H), 9.75 (s, 1H), 9.54 (s, 1H), 8.95 (d, J = 8.2 Hz, 1H), 8.65 (d, J = 8.2 Hz, 1H), 4.1 (m, 12H), 2.3 (m, 12H), 1.2 (m, 18H), −1.52 ppm (br s, 2H). FT-IR (KBr) ν 3465 (ArC−H), 2970, 2924, 2873 (CH), 1294, 1143, 1097 cm^{-1} (SO$_2$). UV/vis (CHCl$_3$) λ_{max} (log ϵ) 705 (5.33), 668 (5.26), 640 (4.1), 610 (4.5), 355 (4.88), 283 nm (4.36). MALDI-TOF MS (dithranol) *m/z* 1276 [M$^+$].

Formylphthalocyanine 6b. A solution of iodophthalocyanine **5b** (40 mg, 0.031 mmol), 4-vinylbenzaldehyde[11] (10 μL, 0.073 mmol), Et$_3$N (0.1 mL), tetra-*n*-butylammonium bromide (11 mg, 0.034 mmol), and Pd(OAc)$_2$ (7.7 mg, 0.034 mmol) in 2 mL of anhydrous DMF was heated at 80 °C for 12 h. After the reaction mixture was cooled to room temperature the solvent was removed under reduced pressure. The solid residue was triturated with methanol/water (3:1), filtered, and purified by chromatography on silica gel with CHCl$_3$/THF (40:1) as eluent. Compound **6b** (20 mg) was obtained as a dark blue solid. Yield: 47%. Mp >250 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.13 (s, 1H), 10.1−9.5 (six s, 6H), 8.95 (br s, 1H), 8.82 (d, J = 8.2 Hz, 1H), 8.31 (d, J = 8.19 Hz, 1H), 8.04 (AA′XX′ system, J = 7.6 Hz, 4H), 7.7, 7.3 (AB system, 2H), 4.1 (m, 12 H), 2.2 (m, 12H), 1.2 ppm (m, 18H). FT-IR (KBr) ν 3441 (ArC−H), 2961, 2921, 2851 (CH), 1715 (C═O), 1607 (C═C), 1292, 1145, 1097 cm^{-1} (SO$_2$). UV/vis (CHCl$_3$) λ_{max} (log ϵ) 692 (5.09), 661 (5.15), 644 (4.67), 600 (4.49), 345 (4.89), 256 nm (4.79). MALDI-TOF MS (dithranol) *m/z* 1383 [M + H]$^+$, 1382 [M$^+$].

Formylphthalocyanine 6c. A solution of tri(*tert*-butyl)iodophthalocyanine[10] (107 mg, 0.12 mmol), 4-vinylbenzaldehyde[11] (16 μL, 0.12 mmol), Et$_3$N (0.1 mL), tetra-*n*-butylammonium bromide (39 mg, 0.12 mmol), and Pd(OAc)$_2$ (1.5 mg, 0.0066 mmol) in anhydrous DMF (3 mL) was heated at 80 °C under argon atmosphere for 12 h. The color changed from blue to green while the reaction proceeded. Afterward, the solvent was evaporated and the solid residue was triturated with methanol/water (3:1), filtered, and purified by column chromatography (SiO$_2$, hexane/dioxane 2:1) to afford 55 mg of **6c**. Yield: 61%. Mp >250 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.2 (s, 1H) 8.4−8.0 (m, 9H), 7.5−7.3 (m, 5H), 7.2 (m, 4H), 1.6 ppm (m, 27H). FT-IR (KBr) ν 3423 (ArC−H), 2955, 2865 (CH), 1697 (CHO), 1595 (C═C), 1488, 1089, 747 cm^{-1}. UV/vis (CHCl$_3$) λ_{max} (log ϵ) 698 (5.21), 683 (5.17), 622 (4.47), 357 (5.0), 293 nm (4.51). MALDI-TOF MS (dithranol) *m/z* 874.3 [M$^+$].

1,3-Diiminoisoindoline 8. A stirred solution of sodium (160 mg, 7.0 mmol) in methanol (120 mL) was cooled to 0 °C in an ice−water bath. 4,5-Bis(propylsulfonyl)phthalonitrile[16] (3.0 g, 8.8 mmol) was then added and ammonia was bubbled through the reaction mixture. After 20 min, the solution became yellowish and TLC showed that there was no unreacted starting material. The solvent was then evaporated and the residue was subjected to column chromatography on silica gel (CHCl$_2$/methanol 9:1). In this way, 1.42 g of compound **8** was isolated as a yellow solid. Yield: 45%. Mp 128−130 °C. ^{1}H NMR (200 MHz, methanol-d_4) δ 8.68 (s, 2H), 3.64 (t, J = 7.0 Hz, 4H), 1.8 (m, 4H), 1.10 ppm (t, J = 7.5 Hz, 6H). ^{13}C NMR (300 MHz, methanol-d_4) δ 143.9, 142.7, 127.6, 108.4, 57.5, 23.3, 14.2 ppm. FT-IR (KBr) ν 3305 (NH), 2926, 2857 (CH), 1678, 1634 (C═N), 1300, 1185, 1145 (SO$_2$), 1101, 655, 588 cm^{-1}. MS (EI) *m/z* 357 [M$^+$], 251 [M − C$_3$H$_7$SO$_2$]$^+$, 144 [M − 2 × C$_3$H$_7$SO$_2$]$^+$.

Calculation of the Mesophase Parameters. a is the lattice parameter of the hexagonal columnar phase ($a = 2/\sqrt{3} \times \langle d_{100}\rangle$ with $\langle d_{100}\rangle = 1/N_{hk}(\sum_{h,k} d_{hk}\sqrt{h^2+k^2+hk})$, and where N_{hk} is the number of *hk0* reflections); density is calculated by using the formula $\rho = M/(VN_A)$, where M is the molar mass (in g) of the molecule (**4**) or the blend, N_A is Avogadro's number, and V is the molecular volume (in cm^3) calculated as $V = a^2c\sqrt{3}/(2 \times 10^{-24})$ (c is the stacking distance, deduced from the outer X-ray scattering halo, corresponding to about 3.4−3.5 Å).

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Supporting Information Available: Copies of the ^{1}H NMR and UV/vis spectra of the Pc-C$_{60}$ dyads **2** and **3**, and their precursors, copies of the MALDI-TOF spectra of the Pc-C$_{60}$ dyads **2** and **3**, synthetic scheme of phthalocyanine **4**, and DSC curves and X-ray diffractograms of the mesophases. This material is available free of charge via the Internet at http://pubs.acs.org.

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