

## New Donor–Acceptor Materials Based on Random Polynorbornenes Bearing Pendant Phthalocyanine and Fullerene Units

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**Abstract:** New donor–acceptor materials based on a polynorbornene framework to which both phthalocyanine and C<sub>60</sub> electroactive pendant units are randomly attached have been prepared in good yield by ring-opening-metathesis polymerization (ROMP) in the presence of a Grubbs catalyst. A structurally related phthalocyanine homopolymer was also synthesized for compar-

ison. A remarkable fluorescence quenching was observed in the homopolymer and accounts for Pc···Pc interactions along the polymeric framework.

**Keywords:** electron transfer · fullerenes · photochemistry · phthalocyanines · ring-opening-metathesis polymerization

As expected, the fluorescence quenching increases in the case of the polynorbornenes containing both Pc and C<sub>60</sub> units owing to photoinduced electron transfer, which was further confirmed by transient absorption spectroscopy. Finally, preliminary solar cell devices made of one of the copolymers were constructed.

### Introduction

Organic solar cells are a promising way towards efficient and low-cost photovoltaic systems that will allow the fabrication of large-area devices.<sup>[1,2]</sup> Organic materials have the advantages of being cheap, easy to process, and the possibility to be deposited on flexible substrates. Both donor-type

semiconducting conjugated polymers (namely, poly-*p*-phenylenevinylenes (PPVs) or poly-3-alkylthiophenes (PATs)) and acceptor-type fullerene derivatives have played a key role in the development of such photovoltaic devices, and up to now power conversion efficiencies of about 5% have been reported.<sup>[3]</sup> However, this research area is still very active, and the perspectives of achieving higher conversion efficiencies for organic solar cells are very optimistic, for instance, by improving solar photon harvesting through new materials whose absorption spectra better match the terrestrial solar spectrum.

In this regard, the incorporation of smaller-bandgap semiconducting polymeric materials and/or organic molecules absorbing in the near-infrared region has become an important task. Among the potential chromophores for this use, phthalocyanines (Pcs)<sup>[4]</sup> present quite unique electronic and optical properties,<sup>[5]</sup> such as an intense absorption in the UV/blue (Soret band) and in the red/near-IR (Q band) spectral regions as well as electrochemical and photochemical stability.

The incorporation of phthalocyanines into photovoltaic devices is usually performed in blends together with semiconductor polymers and/or acceptor molecules such as fullerenes.<sup>[6]</sup> However, the morphological problems of the so-called bulk heterojunctions have suggested the preparation of intrinsically bipolar materials, in which the donor and acceptor photoactive units are covalently linked within the

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same molecule. In this way, a higher concentration of charges within the devices can be produced. Several examples of Pc-C<sub>60</sub> dyads have been described.<sup>[7]</sup> In particular, our groups have focused much effort on the assembly of phthalocyanines and fullerenes and on the study of their electronic interactions.<sup>[8,9]</sup> One of the Pc-C<sub>60</sub> dyads reported by us has even already been applied in a photovoltaic device with very promising results.<sup>[10]</sup>

Either phthalocyanines<sup>[11]</sup> or fullerenes<sup>[12]</sup> have been incorporated within macromolecular frameworks in several cases. For example, Kobayashi and co-workers prepared polymers that contain phthalocyanine pendant units through an olefin-metathesis reaction.<sup>[13]</sup> Ring-opening-metathesis polymerization (ROMP) has been used by the same authors to obtain amphiphilic phthalocyanine block copolymers with the aim of constructing large, stable, ordered phthalocyanine aggregates.<sup>[14]</sup>

However, to the best of our knowledge, only one example of polymeric systems that bear both C<sub>60</sub> and Pc units has ever been reported.<sup>[15]</sup> This scenario stimulated us to prepare C<sub>60</sub>- and phthalocyanine-based donor-acceptor copolymers in order to study the influence of the aggregation properties of polymeric Pc-C<sub>60</sub> systems on their photophysical properties. In particular, we report herein the synthesis, by means of ring-opening-metathesis polymerization (ROMP), of novel poly(norbornene)s **1** and **2** (see Scheme 2), which contain the above-mentioned chromophore units randomly introduced as pendant groups (Figure 1).

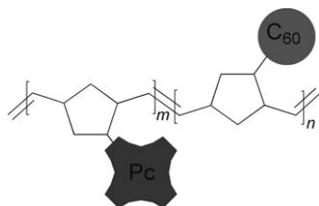


Figure 1. Schematic representation of poly(norbornene)s bearing Pc and C<sub>60</sub> moieties as pendant groups.

#### International Advisory Board Member



**Robert Grubbs** was born in 1972 in Kentucky, USA. He obtained his BS (1963) and MS (1965) at the Univ. of Florida, Gainesville, and completed his PhD (1968) at Columbia Univ., NY. After postdoctoral studies at Stanford Univ., he joined the faculty at Michigan State Univ. (1969). In 1978 he moved to the California Institute of Technology, Pasadena, and is now Victor and Elizabeth Atkins Professor of Chemistry. His research interests lie in organometallic synthesis and catalysis and reagents for olefin metathesis and polymer synthesis. He is the recipient of numerous awards and fellowships and shares the 2005 Nobel Prize in Chemistry with Richard Schrock and Yves Chauvin.

"I envision that Chemistry—An Asian Journal will have the quality of *Angewandte Chemie* and other Wiley-VCH publications."

## Results and Discussion

### Synthesis of Monomers

The C<sub>60</sub>-norbornene and Pc-norbornene monomers **4** and **5**, respectively, were prepared as shown in Scheme 1. A Prato reaction between C<sub>60</sub> and 5-norbornene-2-carboxaldehyde in the presence of sarcosine led to the fulleropyrrolidine-norbornene derivative **4** in 36% yield. Since the commercially available starting aldehyde is actually a mixture of *endo* and *exo* isomers and a new stereocenter is generated, four stereomeric monoadducts **4** are formed. Column chromatography allowed the isolation of two fractions, which were identified by MALDI-TOF spectrometry as the desired monomer **4**. NMR spectroscopy was used to determine the *endo* or *exo* configuration of the two isolated fractions. However, monomer **4** was employed in the subsequent polymerization reactions as a mixture of all the stereoisomers.

On the other hand, the phthalocyanine-norbornene monomer **5** was synthesized by a standard crossover condensation of 4-*tert*-butylphthalonitrile and the dicyano derivative **6** (mixture of *endo* and *exo* isomers), obtained as reported in the literature,<sup>[16]</sup> in the presence of ZnCl<sub>2</sub>. Compound **5** was isolated in 32% yield by column chromatography from the statistical mixture of all the possible phthalocyanines formed. Both monomers were characterized by <sup>1</sup>H NMR, UV/Vis and FTIR spectroscopy, and MALDI-TOF mass spectrometry.

### Synthesis of Poly(norbornene)s

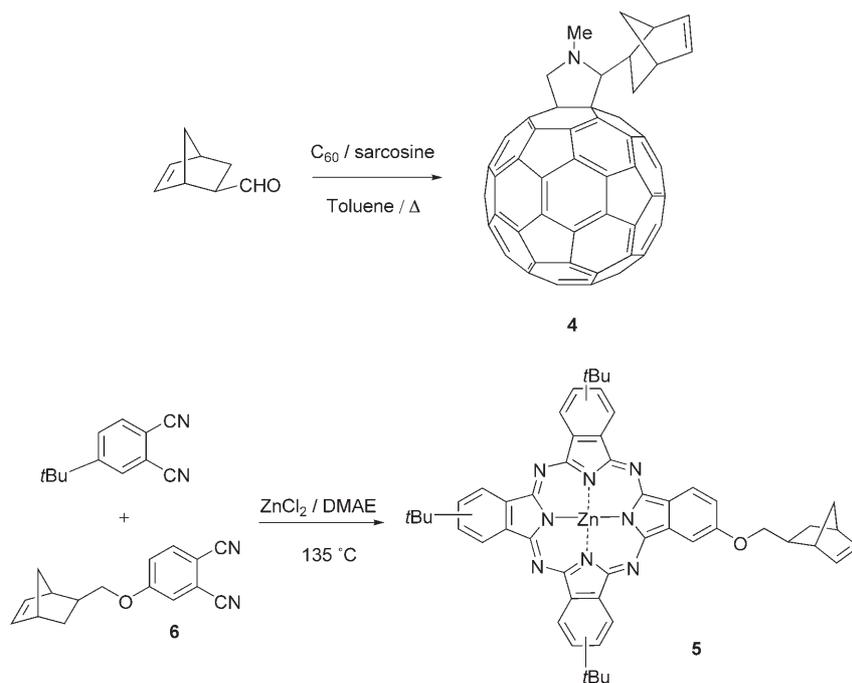
[(1,3-Dimesityl-4,5-dihydroimidazol-2-ylidene)- (PCy<sub>3</sub>)Cl<sub>2</sub>Ru=CHPh], a highly effective Grubbs catalyst that polymerizes different types of strained cyclic olefins,<sup>[17]</sup> was used to prepare copolymers **1** and **2** from different ratios (2:3 and 1:4, respectively) of the appropriate fulleropyrrolidine- and phthalocyanine-norbornene monomers **4** and **5** (Scheme 2 and Table 1). Fullerene/monomer molar ratios higher than 40% were not tried in the feed owing to

Table 1. Polymerization results in toluene at room temperature.

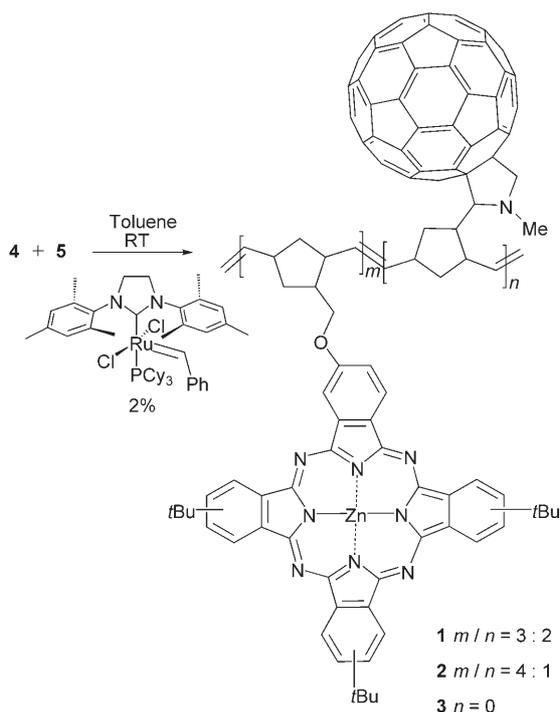
Polymer	4 [mol %]	5 [mol %]	M <sub>n</sub> <sup>[a]</sup>	PDI <sup>[a]</sup>	C60 ratio [%] in the copolymers		
					UV/Vis	FTIR <sup>[b]</sup>	Elemental analysis <sup>[b]</sup>
<b>1</b>	40	60	13 700	2.5	24	31	41
<b>2</b>	20	80	16 100	2.6	8	12	24
<b>3</b>	0	100	16 400	2.2	–	–	–

[a] Polydispersity index determined by gel-permeation chromatography in THF relative to monodisperse polystyrene standards. [b] Determined by intrapolation into a calibration line.

the expected decrease in the solubility of the final copolymer. Homopolymer **3**, which bears only phthalocyanine units, was also prepared for comparison. The polymerizations were carried out at room temperature in dry toluene by following a described procedure.<sup>[18]</sup> The resultant polymers were scarcely soluble in most common organic sol-



Scheme 1. Synthesis of norbornene monomers **4** and **5**. DMAE = *N,N*-dimethylaminoethanol.



Scheme 2. Synthesis of copoly(norbornene)s **1** and **2** and homopoly(norbornene) **3**.

vents, except THF, which allowed us to remove residual monomer and catalyst by subsequent washing with methanol, acetone, ethyl acetate, and chloroform. Further purification by gel-permeation chromatography (GPC) (Bio-Beads SX-

1, 200–400 mesh, eluting with THF) yielded the final pure materials.

Poly(norbornene)s **1–3** were characterized by mass spectrometry, GPC, and by IR and UV/Vis spectroscopy. GPC results (Table 1) show average molecular weights of  $\approx 15000$ <sup>[19]</sup> and polydispersities of 2.2–2.6. MALDI-TOF MS was also used to characterize polymers **1–3**. The spectrum of homopolymer **3** shows sets of peaks at *m/z* 2712 (trimer), 3579 (tetramer), 4444 (pentamer), 5310 (hexamer), 6177 (heptamer), 7045 (octamer), 7912 (nonamer), 8771 (decamer), and 9632 (undecamer).<sup>[20]</sup> Interestingly, the spectra of copolymers **1** and **2** present a set of broad peaks with maxima at similar values (see MALDI-TOF spectrum of copolymer **2** in the Supporting Information), which is reason-

able considering that these polymeric systems are randomly composed of two different monomers whose exact mass differs by 3 units.

UV/Vis spectra of phthalocyanine monomer **5**, phthalocyanine homopolymer **3**, and phthalocyanine-*C*<sub>60</sub> copolymers **1** and **2** in CHCl<sub>3</sub> are collected in Figure 2. The spectrum

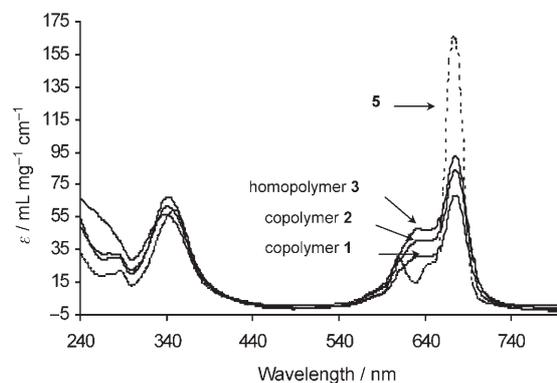


Figure 2. Electronic absorption spectra in THF of copolymers **1** and **2**, homopolymer **3**, and monomer **5**.

corresponding to monomer **5** exhibits an intense sharp Q band at 675 nm, typical of monomeric metallophthalocyanines. In contrast, a new broad blue-shifted absorption centered at about 632 nm is observed in the spectrum of homopolymer **3**, indicative of a certain degree of exciton coupling between adjacent phthalocyanine moieties within the polymeric backbone.<sup>[14]</sup> The same type of broadening occurs for

copolymers **1** and **2**, clearly lowering the intensity of the new band and that of the peak at 675 nm when increasing the fullerene molar ratio in the polymer. The Pc/C<sub>60</sub> molar ratio in the final copolymer could be estimated by plotting a calibration line using the absorbances at 675 nm at different concentrations of homopolymer **3** solutions (see Supporting Information). Intrapolation of the absorbance of a copolymer solution of known concentration should reveal the molar amount of Pc units and, therefore, the molar ratio of both chromophores. Similar experiments have been carried out by using IR spectroscopy (absorbance ratios at  $\tilde{\nu}$ =1611 and 527 cm<sup>-1</sup> were plotted) and elemental analysis, and the results are summarized in Table 1. Besides the appreciable error of the experiments, it can be concluded from all these data that the incorporation of both monomers proceeds randomly, and the molecular composition of the final copolymer corresponds to the molar ratio of each monomer in the feed.

### Photophysical Studies

The ZnPc fluorescence emerged as a powerful probe to pinpoint the excited state interactions between the photoexcited ZnPc electron donor and the C<sub>60</sub> electron acceptor in copolymers **1** and **2**. As a reference, we selected the symmetrical tetra-*tert*-butylZnPc, whose excited state and one-electron-oxidized characteristics are well documented.<sup>[8c]</sup> The fluorescence of the (ZnPc)<sub>n</sub> homopolymer **3** is, relative to the ZnPc model, quenched with factors of about 10 in *ortho*-dichlorobenzene and 50 in THF (Figure 3). Notably, the unexpected quenching is not due to electron-transfer in-

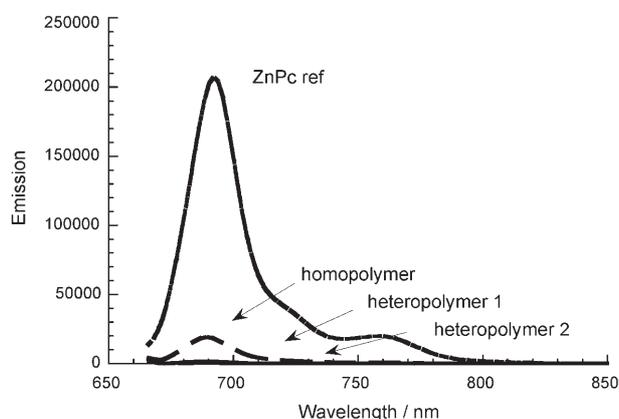


Figure 3. Fluorescence spectra of ZnPc reference, copolymer **1**, copolymer **2**, and homopolymer **3** in oxygenated *ortho*-dichlorobenzene with identical absorption at the 660-nm excitation wavelength.

teractions. Instead, excited-state-chromophore annihilations, which are caused by the high congestion of the ZnPc moieties along the polymer backbone and further augmented by the high affinity of ZnPc moieties to undergo  $\pi$ - $\pi$  stacking, are likely to be responsible for this trend.

Important is the fact that the ZnPc fluorescence in copolymers **1** and **2** is subject to even further quenching (Figure 3). The extent of quenching depends on the relative

ZnPc/C<sub>60</sub> ratio: Increasing the relative C<sub>60</sub> yield (from 80:20 in **2** to 60:40 in **1**) leads to an amplification of the quenching. This trend holds for THF and *ortho*-dichlorobenzene as solvents, but in THF, which is the less polar solvent, the fluorescence quantum yields in copolymers **1** and **2** are about double that in *ortho*-dichlorobenzene.

In time-resolved experiments, the ZnPc reference reveals a monoexponential fluorescence lifetime of 3.1 ns, which is somewhat shorter, but still monoexponential, with a value of 2.6 ns in (ZnPc)<sub>n</sub> homopolymer **3** (both values are measured in *ortho*-dichlorobenzene). In contrast, we found for copolymers **1** and **2** a double-exponential decay behavior. The longer lifetime (i.e., 2.6 ± 0.2 ns) is identical to that measured for homopolymer **3** and represents unquenched ZnPc moieties, whereas the shorter-lived component (i.e., 0.1 ± 0.05 ns) reflects the actual electron-transfer process. Interestingly, the relative weight of the short-lived component increases with C<sub>60</sub> concentration, and is higher in copolymer **1** than in **2**.

Spectroscopic evidence for the electron-transfer fluorescence quenching came from transient absorption measurements following nanosecond excitation at 355 nm of the ZnPc chromophore in the ZnPc reference, (ZnPc)<sub>n</sub> homopolymer **3**, and copolymers **1** and **2**. In the case of the ZnPc reference and the (ZnPc)<sub>n</sub> homopolymer **3**, the ZnPc triplet features are discernable, as they are formed through a rapid intersystem crossing process between the initially formed singlet and triplet manifold. In particular, the most eminent features are transient bleaching between 605 and 705 nm and new absorptions centered at 550 and 740 nm. The differential absorptions changes, recorded following the nanosecond excitation of copolymers **1** and **2**, revealed key features at 860 and 1000 nm (see Figure 4), which correspond to the one-electron-oxidized ZnPc<sup>•+</sup> and one-electron-reduced C<sub>60</sub><sup>•-</sup>. The lifetime of the charge-separated state, as determined at various wavelengths, is 12.6  $\mu$ s. This value is about 4 orders of magnitude longer than those measured for structurally related molecular Pc-C<sub>60</sub> dyads.<sup>[8c]</sup> This leads us to conclude that positive effects—on the photophysical properties of the Pc-C<sub>60</sub> ensembles—evolve from the incorporation of the photoactive units within polymeric frameworks. To our knowledge, this is the first time that such a long-lived Pc<sup>•+</sup>-C<sub>60</sub><sup>•-</sup> state is formed in a fully covalent system.

The photoinduced absorption (PIA) spectrum of drop cast films of copolymer **1** demonstrates that long-lived radical ion pairs (with an average lifetime of 0.4 ms) are formed in the solid state with photons of relatively low energy, which opens up the possibility of using the material for photon harvesting owing to a good match of the absorption spectrum with the terrestrial solar spectrum, which has its maximum photon flux at around 700 nm.

Preliminary solar cells built with copolymer **1** as the active layer have shown only a moderate power-conversion efficiency of  $\approx$ 0.07% under simulated solar illumination (AM 1.5, 100 mW cm<sup>-2</sup>). However, the good match between the photocurrent (IPCE) and the absorption spectra of thin films of copolymer **1** (Figure 5) confirm the ability of the

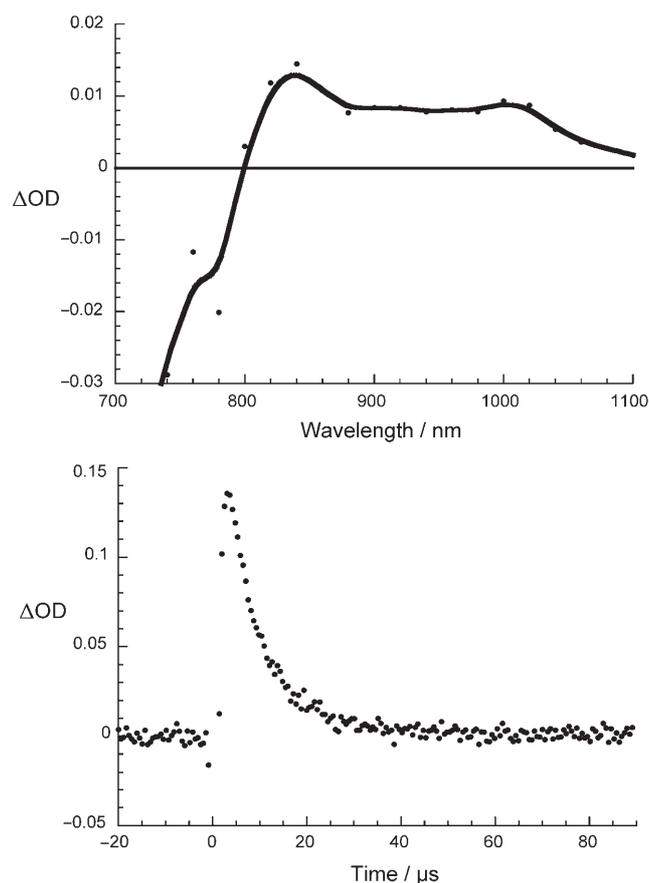


Figure 4. Top: Differential absorption spectra (near-infrared) obtained upon nanosecond flash photolysis (355 nm) of **1** in nitrogen-saturated *ortho*-dichlorobenzene with a time delay of 50 ns. Bottom: Time absorption profile at 840 nm showing the decay of the radical ion pair feature.

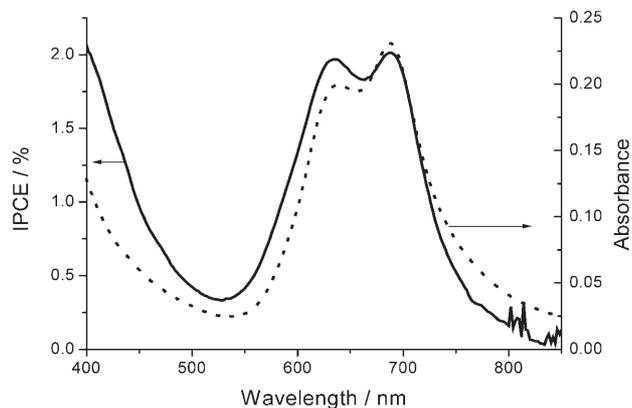


Figure 5. IPCE (incident photon to current efficiency) spectrum of a photovoltaic device with copolymer **1** as the active layer (solid line, left y axis) compared with the absorption spectrum of copolymer **1** (dotted line, right y axis).

material to create charge carriers from absorbed photons with a wavelength of up to 800 nm. Our current investigations are being directed at the optimization of the devices by improving the film morphology. Furthermore, the influence of the donor/acceptor ratio on the performance will

also be studied, as the fullerene content may be too low relative to bulk heterojunction solar cells with conjugated polymers.

## Summary

We have synthesised new donor–acceptor materials for photovoltaic applications. The donor (phthalocyanine) and the acceptor (fullerene) units are covalently linked as pendant groups to a polynorbornene framework. Random copolymers **1** and **2** were formed in good yield through a ring-opening-metathesis reaction from the corresponding phthalocyanine and  $C_{60}$ -norbornene monomers. In contrast to phthalocyanine monomer **5**, the absorption and fluorescence spectra of copolymers **1** and **2** indicated a strong excitonic coupling between phthalocyanine units owing to intramolecular aggregation. Additionally, long-lived charge-separated states formed by photoinduced electron transfer from the donor Pc units to the  $C_{60}$  acceptor units of the copolymers have been detected by means of fluorescence and transient absorption experiments. Finally, preliminary results on the incorporation of the Pc– $C_{60}$  copolymers into photovoltaic devices were described. Although the overall photocurrents and, therefore, the conversion efficiencies are only moderate, it is shown that copolymer **1** can harvest photons with wavelengths up to the infrared region, thus making the material an interesting candidate for low-bandgap photovoltaic devices.

## Experimental Section

### General

Chemicals were purchased from Aldrich and used as received without further purification. Most of the solvents employed were purchased from SDS (<http://www.sds.tm.fr>). Toluene for reactions was dried over 4-Å molecular sieves previously activated by microwaves, and stored under argon before use. The monitoring of the reactions was carried out by thin-layer chromatography (TLC) with aluminum sheets precoated with silica gel 60  $F_{254}$  (Merck). The purification and isolation of most of the products was performed by flash-column chromatography with silica gel Merck-60 (230–400 mesh, 0.040–0.063 mm). Melting points were determined on a Büchi apparatus and are uncorrected. Infrared spectra were recorded on a Bruker (FT-IR) spectrophotometer. The  $^1H$  NMR spectra were recorded on a Bruker AC-200 (200 MHz) and AC-300 (300 MHz). UV/Vis spectra were recorded on a Perkin-Elmer 8453 and a spectrophotometer. The mass spectra were determined on a VG AutoSpec spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. GPC analyses were carried out with a HPLC system using an Altex model 110 A pump, a Rheodyne model 7125 injector with a 100  $\mu$ L loop, 10  $\mu$ m bed columns, and a Knauer differential refractometer using THF as the eluent. The flow rate was set to 1.0  $mL\ min^{-1}$ , and molecular weights and polydispersities were reported relative to monodispersed polystyrene standards (obtained from American Polymer Standards Inc.).

**4** (mixture of stereoisomers): *N*-Methylglycine (62 mg, 0.695 mmol) and  $C_{60}$  (100 mg, 0.139 mmol) were dissolved in dry toluene (40 mL) and heated at 60°C. A solution of 5-norbornene-2-carboxaldehyde (*endolexo* 1.9:1) (0.55 mL, 0.139 mmol) in dry toluene (15 mL) was added, and the resultant mixture was heated at 110°C for 12 h. The solvent was cooled and evaporated under reduced pressure. The crude solid material was pu-

rified by column chromatography on silica gel with toluene/THF (50:1) as eluent. The two first brown fractions were collected and yielded **4** as a dark brown solid (36%). M.p. > 250 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, TMS) (*endo* isomer): δ = 6.4 (m, 2H; vinyl H), 4.97 (d, *J* = 11.73 Hz, 1H; pyrrolidine), 4.74 (d, *J* = 11.73 Hz, 1H; pyrrolidine), 4.23 (d, *J* = 11.13 Hz, 1H; pyrrolidine), 3.56 (s, 3H; NCH<sub>3</sub>), 3.20 (m, 1H; CH), 2.93 (br s, 1H; CH), 2.20 (m, 1H; CH), 1.6 (m, 1H; CH<sub>2</sub>), 1.40–1.20 (m, 2H; CH<sub>2</sub>), 0.9 ppm (m, 1H; CH); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, TMS) (*exo* isomer): 6.20 (m, 2H; vinyl H), 5.00 (d, *J* = 11.73 Hz, 1H; pyrrolidine), 4.87 (d, *J* = 11.73 Hz, 1H; pyrrolidine), 4.72 (d, *J* = 11.16 Hz, 1H; pyrrolidine), 3.57 (s, 3H; NCH<sub>3</sub>), 3.30 (m, 1H; CH), 3.00 (br s, 1H; CH), 2.10 (m, 1H; CH), 1.80 (m, 1H; CH<sub>2</sub>), 1.40–1.20 (m, 2H; CH<sub>2</sub>), 0.9 ppm (m, 1H; CH). IR (KBr):  $\tilde{\nu}$  = 3421 (ArCH), 2918, 2848 (CH), 1622 (C=C), 1456, 1421 (C–N), 711, 526 cm<sup>-1</sup>; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  (log  $\epsilon$ ) = 260 (4.86), 320 (4.49), 430 nm (3.43); MALDI-TOF MS: *m/z*: 869 [M<sup>+</sup>]; elemental analysis: calcd (%) for C<sub>70</sub>H<sub>15</sub>N (869.12): C 96.57, H 1.72, N 1.61; found: C 96.62, H 1.72, N 1.75.

**5**: A mixture of 6<sup>[15]</sup> (*endo/exo* 1.6:1) (250 mg, 1 mmol), 4-*tert*-butylphthalonitrile (1 g, 5.4 mmol) and ZnCl<sub>2</sub> (204 mg, 1.5 mmol) in *N,N*-dimethylaminoethanol was heated overnight at reflux under argon. The mixture was cooled, triturated with methanol/water (3:1), and the precipitate was filtered. The residue was purified by column chromatography (silica gel, hexane/dioxane 4:1) to give a blue solid (32%). M.p. > 250 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 8.8–7.8 (m, 12H; arom. H), 6.2–6.0 (m, 2H; vinyl H), 4.0–3.6 (m, 2H; CH<sub>2</sub>O), 3.1–3.0 (m, 2H; CH), 2.8 (m, 1H; CH<sub>2</sub>), 2.0 (m, 1H; CH<sub>2</sub>), 1.8 (m, 27H; CH<sub>3</sub>), 1.2 (m, 3H; CH<sub>2</sub>), 0.1 (m, 1H; CH<sub>2</sub>); IR (KBr):  $\tilde{\nu}$  = 3425 (ArCH), 2952, 2900, 2862 (CH), 1608 (C=C), 1488, 1089, 746 cm<sup>-1</sup>; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  (log  $\epsilon$ ) = 352 (4.7), 610 (4.39), 673 nm (5.15); MALDI-TOF MS: *m/z*: 866 [M<sup>+</sup>]; elemental analysis: calcd for C<sub>52</sub>H<sub>50</sub>N<sub>8</sub>OZn (866.34): C 71.86, H 5.76, N 12.89; found: C 71.50, H 5.71, N 12.99.

General procedure for polymerization: The appropriate amount of monomers **4** and **5** (or only **5**) and catalyst [1,3-dimesityl-4,5-dihydroimidazol-2-ylidene](PCy<sub>3</sub>)Cl<sub>2</sub>Ru = CHPh]<sup>[21]</sup> (2 mol%) were placed in a dry, argon-filled flask and dissolved in degassed toluene. The solution was stirred for 8 h at room temperature. The solvent was evaporated, and the solid residue sequentially washed with methanol, acetone, ethyl acetate, and chloroform. Further purification by gel-permeation chromatography (Bio-Beads SX-1, THF) gave the corresponding poly(norbornene)s.

**1**: A 40:60 molar ratio of monomers **4** and **5** was used, 66% yield. M.p. > 250 °C; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 343 (56), 632 (30.8), 677 nm (67.6 mL mg<sup>-1</sup> cm<sup>-1</sup>); MALDI-TOF MS: 1846 (dimer), 2716 (trimer), 3586 (tetramer), 4451 (pentamer), 5329 (hexamer), 6198 (heptamer), 7042 (octamer), 7912 (nonamer); IR (KBr):  $\tilde{\nu}$  = 3421 (ArCH), 2948, 2898, 2856 (CH), 1606 (C=C, Pc), 1485, 1087, 746 (Pc), 1456 (C–N, C<sub>60</sub>), 526 cm<sup>-1</sup> (C<sub>60</sub>); elemental analysis: C 78.44, N 8.25.

**2**: A 20:80 molar ratio of monomers **4** and **5** was used, 68% yield. M.p. > 250 °C; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 343 (61.3), 632 (40.4), 677 nm (83.3 mL mg<sup>-1</sup> cm<sup>-1</sup>); MALDI-TOF MS: 1830 (dimer), 2698 (trimer), 3565 (tetramer), 4433 (pentamer), 5301 (hexamer), 6174 (heptamer), 7038 (octamer), 7910 (nonamer), 8762 (decamer); IR (KBr): identical to that of **1**; elemental analysis: C 72.80, N 10.20.

**3**: Only monomer **5** was used, 65% yield. M.p. > 250 °C; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 345 (66.3), 632 (47.6), 677 nm (91.2 mL mg<sup>-1</sup> cm<sup>-1</sup>); MALDI-TOF MS: *m/z*: 2712 (trimer), 3579 (tetramer), 4444 (pentamer), 5310 (hexamer), 6177 (heptamer), 7045 (octamer), 7912 (nonamer), 8771 (decamer), 9632 (undecamer); IR (KBr):  $\tilde{\nu}$  = 3417 (ArCH), 2950, 2898, 2858 (CH), 1608 (C=C), 1487, 1087, 746 cm<sup>-1</sup>; elemental analysis: C 71.05, N 13.05.

#### Photophysical Studies in Solution

Nanosecond laser-flash-photolysis experiments were performed with laser pulses from a Moletron UV-400 nitrogen laser system (337.1 nm, 8 ns pulse width, 1 mJ pulse<sup>-1</sup>) or from a Quanta-Ray CDR Nd:YAG system (355 nm, 20 ns pulse width). The photomultiplier output was digitized with a Tektronix 7912 AD programmable digitizer. For all photophysical experiments an error of 10% must be considered. Fluorescence lifetimes were measured with a Laser Strobe Fluorescence Lifetime Spec-

trometer (Photon Technology International) with 337-nm laser pulses from a nitrogen laser fiber coupled to a lens-based T-formal sample compartment equipped with a stroboscopic detector. Details of the Laser Strobe systems are described on the manufacturer web site: <http://www.pti-nj.com>. Emission spectra were recorded with a SLM 8100 spectrofluorometer. The experiments were performed at room temperature. When measuring the ZnPc emission in the 700-nm region, a 570-nm long-pass filter in the emission path was used in order to eliminate the interference from the solvent and stray light for recording the fullerene fluorescence. Each spectrum was an average of at least five individual scans, and the appropriate corrections were applied.

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