# Solution Self-Assembly and Photophysics of Platinum Complexes Containing Amphiphilic Triblock Random Copolymers Prepared by ROMP

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Ring-opening metathesis polymerization was used to synthesize amphiphilic, phosphorescent block copolymers that self-assemble into nanometer-scaled aggregates when dissolved in a selective solvent. The triblock random copolymer architecture is built up by using an oligoglycol-substituted norbornene derivative for the hydrophilic part, 2,3-norbornenedicarboxylic acid dimethyl ester, as the first segment of the hydrophobic part and a statistical segment made using norbornene-functionalized dyes as the second segment of the hydrophobic part. The dyes comprise a blue fluorescent carbazole derivative serving as the host and a red phosphorescent platinum complex serving as the guest material. Emission properties of the amphiphilic triblock random copolymer dissolved in a nonselective solvent are exclusively determined by the host material. Only blue emission of the carbazole-derivative can be observed. When the polymer is dissolved in a selective solvent, polymer aggregates are formed and energy transfer occurs. In this case, deep red phosphorescence stemming from the platinum complex used as guest component can be observed. The amphiphilic triblock random copolymer architecture allows for the dispersion of the platinum chromophore in a solvent in which the parent chromophore is insoluble, the realization of a large Stokes shift of about 260 nm and significant suppression of platinum complex self-quenching, resulting in considerable phosphorescent quantum yields. Absorbance, luminescence, quantum yield, and lifetime measurements of this polymer and several model polymers in selective and unselective solvents as well as in the solid state have been performed to understand the energy transfer from the host to the guest dye in this particular system.

## Introduction

Phosphorescent cyclometalated platinum(II) complexes continue to be intensively investigated due to their interesting and useful photophysical properties.<sup>1,2</sup> These complexes show significant absorption bands in the visible range and have a relatively large Stokes shift and long luminescence lifetimes.<sup>3</sup> Application in phosphorescent devices, such as chemical sensors,<sup>4</sup> organic light emitting devices (OLEDs),<sup>5</sup> and photovoltaics,<sup>6</sup> often requires the use of a host material, which has to be selected carefully, e.g., in terms of providing efficient Förster energy transfer to name one important prerequisite. The crucial issue is that the triplet energy level of the host must be higher than the triplet energy level of the emitting dopant guest.<sup>7</sup> To reduce quenching effects associated with triplet—triplet annihilation, the phosphorescent dyes are normally dispersed in a conductive polymer host. However, these blend systems are prone to undergo phase separation.<sup>8</sup> Covalent incorporation of the guest into the host-polymer, by contrast, prevents phase separation, leads to higher efficiencies, and constitutes a further step toward an easy and reliable processing of the material.<sup>9,10</sup> Covalent attachment to amphiphilic block copolymers that self-assemble on the nanoscale, in particular, opens up a pathway toward the design of functional materials with complex struc-

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tures and novel properties. The self-assembly behavior of block copolymers has, therefore, become of increasing interest within various sub-areas of materials research,<sup>11</sup> such as electronic applications,<sup>12</sup> drug delivery,<sup>13</sup> and separation and dispersant technologies.<sup>14,15</sup> Compared to small-molecule amphiphilic micelles, block copolymer assemblies show increased stability<sup>16</sup> and high guest encapsulation ability.<sup>17</sup> The major advantage of block copolymers, however, is that one can adjust not only the chemical nature of the blocks but also the molecular characteristics (composition, molecular weight, functional groups) and consequently the size and structure of the aggregates.<sup>17,18</sup> Attachment of metal complexes to amphiphilic block copolymers allows the hybridization of the intrinsic properties of the metal complex (e.g., photophysical properties) with the selfassembly behavior of the block copolymer, taking a further step toward the design of "smart materials".<sup>19,20</sup> Herein, the preparation, characterization, and self-organization of amphiphilic triblock random copolymers containing a blue fluorescent host and a red phosphorescent guest are described. As the polymerization method, ring-opening metathesis polymerization (ROMP) was used because highly functional group tolerant initiators enable a straightforward preparation of well-defined, functionalized polymers.<sup>21</sup> Moreover, ROMP allows for the preparation of block copolymers via "living polymerization".<sup>22,25</sup> The decisive influence of the polymer architecture on the function,

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i.e., (a) the dispersion of the platinum chromophore in a solvent in which the parent chromophore is insoluble, (b) the realization of a large Stokes shift of about 260 nm, and (c) the significant suppression of platinum complex aggregation and, thus, considerable gain of phosphorescent quantum yield, will be discussed in detail.

## **Results and Discussion**

Synthesis. The polymerizable Pt(II) complex 3 was prepared in a three-step procedure. First, the precursor  $\kappa^2(N,C^2)$ -(11-(2phenylpyridine-3-yloxy)undecan-1-ol)- $\kappa^{1}(N)$ -(11-(2-phenylpyridine-3-yloxy)undecan-1-ol)chloroplatinum(II) (2a) was prepared similar to a literature procedure<sup>23</sup> using 11-(2-phenylpyridin-3-yloxy)undecan-1-ol (1c) (for synthesis and preparation of 11-(2-phenylpyridine-3-yloxy)undecan-1-ol see the Supporting Information) and K<sub>2</sub>PtCl<sub>4</sub> as the starting materials. 2a was subsequently reacted with 5-formyl-8-hydroxyquinoline<sup>24</sup> in degassed CH<sub>2</sub>Cl<sub>2</sub>/EtOH and K<sub>2</sub>CO<sub>3</sub> at room temperature using a method similar to that described in the work of Brooks et al.<sup>23</sup> Purification was accomplished by flash chromatography on silica (CH<sub>2</sub>Cl<sub>2</sub>, then acetone;  $R_f = 0.74$ ), yielding **2b** as an orange solid (39%), which, in the third step, was esterified with in situ generated norbornene-2-acid chloride, vielding upon workup the polymerizable complex 3 (cf. Scheme 1).

A similar esterification reaction of 11-[3,6-di(4-formylphenyl)-9*H*-carbazol-9-yl]undecan-1-ol (**5**) was used to prepare monomer **6**. For the formation of the core unit **5**, a Suzuki crosscoupling protocol was used. Precursor **4c**, which was prepared via a hydroboration reaction of 3,6-dibromo-9-(undec-10-enyl)-9*H*-carbazole (**4b**), was reacted with 4-formylphenylboronic acid and Na<sub>2</sub>CO<sub>3</sub> in a mixture of degassed toluene/EtOH/H<sub>2</sub>O in the presence of the catalyst Pd(PPh<sub>3</sub>)<sub>4</sub> at 90 °C for 20 h. The raw product was purified by flash chromatography on silica (Cy/ EA = 5:1,  $R_f$  = 0.52 in Cy/EA = 1:1), yielding a yellow solid (29%) (cf. Scheme 2). Monomers **3** and **6** were isolated and used as a mixture of their corresponding *endo* and *exo* isomers. Monomers were characterized by NMR and IR spectroscopy and elemental analysis (cf. Supporting Information).

The amphiphilic triblock random copolymers **poly b-1**, **poly b-2**, and **poly b-3** were synthesized using a modified "secondgeneration Grubbs" initiator (**G**) by stepwise polymerization of each block (Scheme 3).<sup>25</sup> As building blocks, norbornene derivatives with an ester anchor group were chosen. The anchor group significantly influences the initiation and propagation rates and consequently the polydispersity, as well as the molecular weight of the polymers.<sup>26</sup> Therefore, only monomers with the same anchor group were used.

Compound 7 was chosen as the hydrophobic monomer, while *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid bis[2-[2-(2-ethoxyethoxy]ethoxy]ethyl] ester ( $\mathbf{8}$ )<sup>27</sup> was used for the preparation of the hydrophilic block. An overall polymer length of 300 repeating units was targeted, while the molar ratio of the hydrophobic block to the hydrophilic block was kept constant at 2:1. Finally, a third segment was copolymerized using a mixture of 3 equiv of **3** and 17 equiv of **6**. Thus, the

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Scheme 1. Synthesis of the Polymerizable Pt Complex  $3^a$ 



<sup>*a*</sup> Reagents and conditions: (a) 11-bromoundecan-1-ol,  $K_2CO_3/NaOH = 1:1$ , 2-butanone, 90 °C, 24 h (75%); (b) phenylboronic acid, Pd(PPh\_3)\_4,  $K_2CO_3$ , toluene/EtOH/H<sub>2</sub>O = 1:1:1, 95 °C, 24 h (94%); (c)  $K_2PtCl_4$ , ethoxyethanol/H<sub>2</sub>O = 3:1, 80 °C, 21 h (46%); (d) 5-formyl-8-hydroxyquinoline, CH<sub>2</sub>Cl<sub>2</sub>/EtOH = 1:1,  $K_2CO_3$ , RT (73%); (e) cyclopentadiene, acryloyl chloride, CH<sub>2</sub>Cl<sub>2</sub>, RT, 12 h, then pyridine, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, RT (51%).

Scheme 2. Synthesis of the Polymerizable Carbazole Host Material 6<sup>*a*</sup>



<sup>*a*</sup> Reagents and conditions: (a) 11-bromoundec-1-ene, NaOH, DMSO/H<sub>2</sub>O, 70 °C, 20 h (89%); (b) BH<sub>3</sub>•THF, THF, RT, 12 h (82%); (c) 4-formylphenylboronic acid, Na<sub>2</sub>CO<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene/EtOH/H<sub>2</sub>O, 90 °C, 20 h (29%); (d) cyclopentadiene, acryloyl chloride, CH<sub>2</sub>Cl<sub>2</sub>, RT, 12 h, then DMAP, pyridine, 0 °C, 30 min, RT, 24 h (47%).

third segment exhibits a random distribution of repeating units comprising a platinum complex and a carbazole unit. Using the reaction conditions described in the caption of Scheme 3 followed by repeated precipitation of  $CH_2Cl_2$  solutions from *n*-pentane gave **poly b-1** in 63% yield.

Similarly, two reference triblock random copolymers **poly b-2** and **poly b-3** were prepared by varying the last randomly composed segment (cf. Figure 1). In the case of **poly b-2**, the last segment was built up using 17 equiv of **7** and 3 equiv of **3**; that is, no carbazole-bearing monomer was used. In the case of **poly b-3**, the platinum-bearing monomer was replaced by monomer **6** (3 equiv). Both polymers were isolated in 75% yield.

The block polymer composition was verified by <sup>1</sup>H NMR spectroscopy in a nonselective solvent (CDCl<sub>3</sub>) via integration of the multiplet at 5.58-5.10 ppm, representing the polymer double bond and the triplet at 1.20 ppm, representing the methyl groups of monomer 8. By evaluation of the integrals an amount of about  $33\% \pm 3\%$  of 8 was determined, which was consistent for **poly b-1**, **poly b-2**, and **poly b-3**. Integrals of the peaks at 10.01, 8.37, 7.91-7.82, 7.46, and 7.05 ppm characteristic for the carbazole moiety confirmed the successful incorporation of 6. NMR spectroscopic evidence for the incorporation of 3 could not be gained, due to the minute ratio (<1 mol %) of 3. However, complete polymerization of 3 and 6 can be assumed

from the results obtained by TLC control of the reaction progress. Gel permeation chromatography (GPC) of **poly b-1** in THF relative to polystyrene standards revealed a polydispersity index (PDI) of 1.53 and a number average molecular weight ( $M_n$ ) of 75 100 g/mol. Corresponding data for **poly b-2** and **poly b-3** were similar (**poly b-2**: PDI = 1.23,  $M_n = 61100$  g/mol and **poly b-3**: PDI = 1.24,  $M_n = 70200$  g/mol) and underline the reliability of the polymerization method.

Aggregate Preparation and Characterization. As reported previously,<sup>27</sup> MeOH is a selective solvent for the oligoglycolfunctionalized segment of the triblock random copolymer and therefore suited for promoting the self-assembly of the material in solution. A dispersion of polymer aggregates was obtained by simply stirring 0.1 wt % of the corresponding polymer in methanol under ambient conditions for 18 h. The formation of aggregates in MeOH was ensured by NMR spectroscopy and dynamic light scattering (DLS). <sup>1</sup>H NMR spectra were recorded in CD<sub>3</sub>OD and compared to those obtained from CDCl<sub>3</sub> solutions. Representative results are discussed for **poly b-1** (Figure 2). Whereas characteristic carbazole signals could be observed in the spectrum recorded in CDCl<sub>3</sub>, these signals were not detected when CD<sub>3</sub>OD was used as the solvent. These results suggest that the segment comprising both dyes forms the cores





<sup>*a*</sup> Reagents and conditions: (a) **8** and **G** in dry and degassed  $CH_2Cl_2$ , RT, 2 h, then addition of **7**, RT, 1 h, then addition of a mixture of **3** and **6**, RT, 1 h, then addition of ethyl vinyl ether (excess), RT, 1 h (63%).

of the aggregates.<sup>28</sup> Further evidence for this hypothesis was retrieved by evaluation of the integral ratio for the peaks representing the polymer backbone's double bonds (signal ranging from 5.51 to 5.19 ppm) and the signal assigned to the COOCH<sub>2</sub> group (peaking at 4.19 ppm). In CDCl<sub>3</sub> this ratio was determined to be 2:1.2, while in CD<sub>3</sub>OD a ratio of 2:4 was revealed. The ratio obtained from the CD<sub>3</sub>OD spectra corresponds to the theoretically expected value for a homopolymer of monomer **8** and constitutes a strong indication for the presence of aggregates with a shell composed of the oligoglycolbearing segment of the triblock random copolymer.

The block copolymer aggregates were characterized by dynamic light scattering using a Malvern ZetaSizer NanoZS equipped with a 633 nm laser. Measurements were performed at 20 °C. A summary of the particle sizes in methanol is given in Table 1. All triblock random copolymers under investigation formed aggregates in MeOH with diameters ranging from 81 to 88 nm. Monomodal size distributions with narrow PDI<sub>DLS</sub> values (0.03–0.09) were obtained in all cases.

**Photophysical Properties.** Optical properties of the amphiphilic triblock random copolymers **poly b-1**, **poly b-2**, and **poly b-3** were investigated by UV/vis absorption and photoluminescence spectroscopy; excitation spectra complement the



**Figure 1.** Depiction of **poly b-2** (molar equiv: **8**:**G**:**7**:**3**:**7** = 100: 1:200:3:17) and **poly b-3** (molar equiv: **8**:**G**:**7**:**6**:**7** = 100:1:200:3: 17).



Figure 2. <sup>1</sup>H NMR spectra of poly b-1 in CD<sub>3</sub>OD and CDCl<sub>3</sub>.

Table 1. Aggregate Sizes of Triblock Random Copolymers in Methanol Determined by DLS;  $M_n$ 's as well as PDIs Determined from GPC Measurements

polymer	diametera [nm]	PDI <sub>DLS</sub>	$M_n^b$ [g/M]	$PDI^{b}$
poly b-1	88	0.09	75 100	1.53
poly b-2	81	0.03	61 100	1.23
poly b-3	81	0.06	70 200	1.24

<sup>*a*</sup> Determined by dynamic light scattering at 20 °C; 0.1 wt % in methanol. <sup>*b*</sup> Determined by GPC with THF as the solvent; calibrated against polystyrene standards.

results. Emphasis is given to the comparison of the photophysical properties in a selective solvent, i.e., MeOH and a nonselective solvent, namely,  $CHCl_3$ . Photophysical data of monomers **3** and **6** were established for comparison and completeness. Furthermore, data from thin films of the materials and measure-

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Figure 3. Absorption and emission spectra of 3, 6, and poly b-1 measured in CHCl<sub>3</sub> at RT. Absorption:  $\blacksquare = 3$ ,  $[3] = 2.1 \times 10^{-5}$  M ( $\lambda_{max} = 468$  nm);  $\blacktriangle = 6$ ,  $[6] = 2.2 \times 10^{-5}$  M ( $\lambda_{max} = 361$  nm);  $\blacklozenge = poly$  b-1,  $[poly b-1] = 1.4 \times 10^{-1}$  mg/mL ( $\lambda_{max} = 361$  nm). Fluorescence:  $\square = 3$ ,  $[3] = 4.9 \times 10^{-6}$  M ( $\lambda_{ex} = 467$  nm);  $\triangle = 6$ ,  $[6] = 3.9 \times 10^{-8}$  M ( $\lambda_{ex} = 360$  nm);  $\bigcirc = poly$  b-1,  $[poly b-1] = 4.5 \times 10^{-2}$  mg/mL ( $\lambda_{ex} = 360$  nm).

ments of quantum yields and luminescence lifetime of the phosphorescent dyes under various conditions will be presented.

The absorption spectrum of complex 3 measured in diluted solution of  $\hat{CHCl}_3$  ([3] = 2.1 × 10<sup>-5</sup> M) at room temperature under ambient conditions showed a significant absorption band in the visible region. This lowest energy absorption band is centered at 468 nm, with an extinction coefficient of  $13.1 \times$  $10^3 \text{ cm}^{-1} \text{ M}^{-1}$  and can be assigned to an intraligand charge transfer transition (ILCT) of the coordinated quinolinolate ligand.<sup>3</sup> Complex **3** emitted red light with its maximum at 621 nm ( $\lambda_{ex} = 468$  nm) in CHCl<sub>3</sub> solution. The absorption feature of 3 peaking at 468 nm matches favorably with the emission at 453 nm ( $\lambda_{ex} = 360$  nm) of monomer **6**, which exhibits its lowest energy absorption maximum at 361 nm. Thus, efficient energy transfer from the host (carbazole derivative 6) to the guest (platinum complex 3) can be anticipated (cf. Figure 3). It is worth mentioning that several similar carbazole-based dyes bearing different substituents at the 3- and 6-positions are not suited as host materials because of less favorable photophysical properties.7,29,30

The block copolymer **poly b-1** exhibited the characteristic carbazole absorption bands at 246, 315, and 361 nm, as well as a weak absorption band at 467 nm, attributed to the incorporated platinum chromophore. The emission maximum of **poly b-1** in CHCl<sub>3</sub> with  $\lambda_{max} = 450$  nm ( $\lambda_{ex} = 360$  nm) is very similar to the emission maximum of the monomer **6** in CHCl<sub>3</sub> ( $\lambda_{max} = 453$  nm); thus no energy transfer to the phosphorescent platinum dye occurred under these conditions. In sharp contrast, a solution of aggregated **poly b-1** in methanol exhibited bright red luminescence with its emission maximum peaking at 625 nm ( $\lambda_{ex} = 370$  nm). In this case, efficient energy transfer from the carbazole host to the platinum guest occurred, whereas host

emission (weak and broad emission band from 440 to 520 nm) was negligible (cf. Figure 4). In addition, the corresponding excitation spectrum recorded in methanol (for an emission wavelength ( $\lambda_{exc}$ ) of 625 nm) supports the feasibility of the energy transfer. Two prominent peaks were observed. The more dominant excitation band at 370 nm characterizes the carbazole moiety; the weaker band at 480 nm belongs to the platinum dye (cf. Supporting Information).

DLS measurements of the diluted MeOH samples, previously used for spectroscopic measurements, confirmed the presence of block copolymer aggregates. Particle sizes nicely resembled those obtained from solutions of higher concentration (cf. Table 1). The occurrence of energy transfer in MeOH but not in CHCl<sub>3</sub> might be simply explained by the fact that in the aggregates a "solid state like" environment is created<sup>31</sup> and the distance between host and guest is reduced.<sup>32</sup> Maximized spectral overlap between the donor emission and the acceptor absorption, improved orientation, and a shortened distance between the donor and the acceptor should lead to more efficient FRET.<sup>33</sup> To support this hypothesis, a thin film of **poly b-1** was prepared by drop-casting a methanolic solution onto glass and examining its photophysical properties. Surprisingly, considerable host emission peaking at 437 nm in addition to the expected guest emission peaking at 625 nm was observed under these conditions (cf. Figure 4). This observation might be explained by either an increased luminescence quantum yield of the host material in the solid state or a less efficient energy transfer in the film. The latter might be ascribed to the tendency of square-planar platinum chromophores to form aggregates and excimers in

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Figure 4. Absorption ( $\bullet$ ), excitation ( $\blacksquare$ ), and emission ( $\Box$ ) spectra of poly b-1 measured in MeOH and thin film excitation ( $\blacktriangle$ ) and emission ( $\Delta$ ) spectra of a drop-casted film on glass of poly b-1 from MeOH (2 mg mL<sup>-1</sup> copolymer) ( $\lambda_{ex} = 370$  nm,  $\lambda_{exc} = 625$  nm). Absorption in MeOH: [poly b-1] =  $1.0 \times 10^{-1}$  mg/mL. Excitation in MeOH: [poly b-1] =  $3.4 \times 10^{-2}$  mg/mL ( $\lambda_{exc} = 625$  nm). Emission in MeOH: [poly b-1] =  $3.4 \times 10^{-2}$  mg/mL ( $\lambda_{exc} = 370$  nm).

concentrated solutions as well as in the solid state.<sup>2,34–36</sup> Since the aggregation of the platinum dyes can also affect the energies of the acceptor states, a different spectral overlap with the corresponding host system can be anticipated. The latter includes interactions that involve overlap of the  $d_{z^2}$  orbitals, which frequently lead to  $d\sigma^*(Pt_2) \rightarrow \pi^*(\text{ligand})$  (metal-metal to ligand charge transfer, MMLCT) excited states These low-energy excited states result in more red-shifted spectra compared to mononuclear absorption.<sup>37</sup>

Aggregate formation in this particular system was studied using model polymer **poly b-2** (cf. Figure 1). The emission spectrum of **poly b-2** in CHCl<sub>3</sub> exhibited the same emission maximum (623 nm) as the platinum monomer **3** in CHCl<sub>3</sub> (621 nm). By contrast, the emission spectrum of **poly b-2** in methanol showed only a very weak emission with three major emission bands at 586, 631, and 708 nm, which is a strong indication for aggregation of the platinum dyes.<sup>34,35</sup>

Aggregation was further studied by photoluminescence quantum yield (PLQY) and lifetime measurements ( $\tau$ ) in solution. Quantum yields of the corresponding compounds were measured in aerated as well as degassed CHCl<sub>3</sub> and MeOH solutions using 4-dicyanomethylene-2-methyl-6-(4-(dimethyl-amino)styryl)-4*H*-pyran (DCM) as the standard.<sup>38</sup> Quenching by oxygen was determined by measuring the luminescence lifetime in aerated and degassed solutions of CHCl<sub>3</sub> and MeOH using a frequency-based method.<sup>39</sup> Results are presented in Table 2.

PLQY in degassed CHCl<sub>3</sub> solution of the platinum monomer 3 showed slight concentration dependence, ranging from 5.2  $\pm$ 

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 Table 2. PLQY and Lifetimes of poly b-1, poly b-2, and the

 Platinum Monomer 3

polymer	conc of 3 [mg/mL]	$ au_{ m air} \ [\mu { m s}]^a$	$ au_{ m N2} \ [\mu  m s]^a$	PLQY air [%]	PLQY N <sub>2</sub> [%]
poly b-1 <sup>c</sup>	$3.2 \times 10^{-3}$ $3.4 \times 10^{-3}$	$11 \pm 1$ 2 + 1	$14 \pm 1$ 6 ± 1	$3.3 \pm 0.5$	$4.4 \pm 0.5$
poly b-2 poly b- $2^d$ $3^d$	$7.2 \times 10^{-4}$ $1.1 \times 10^{-3}$	$5 \pm 2$ $3 \pm 2$	$19 \pm 2$ $30 \pm 2$	$0.2 \pm 0.2 \\ 0.2 \pm 0.2$	$1.1 \pm 0.5 \\ 7.6 \pm 1$

<sup>*a*</sup> Apparent lifetimes measured at a modulation frequency of 5.5 kHz (for PLQY measurements  $\lambda_{ex} = 470$  nm was applied). <sup>*b*</sup> PLQY could not be determined (broad excimer emission). <sup>*c*</sup> Measured in MeOH. <sup>*d*</sup> Measured in CHCl<sub>3</sub>.

1% (1.1 × 10<sup>-2</sup> mg/mL) to 7.6 ± 1% (1.1 × 10<sup>-3</sup> mg/mL). The increase of quantum yields at higher dilutions indicates selfquenching at higher concentrations.<sup>3,40</sup> Luminescence lifetime of **3** in CHCl<sub>3</sub> ranged from  $1 \pm 1$  to  $3 \pm 1 \mu$ s in aerated solutions and from 23  $\pm$  1  $\mu s$  to 30  $\pm$  1  $\mu s$  in degassed solutions. The PLQY of the triblock random copolymer poly b-1 (2.3 wt % of 3) was determined to be 4.4  $\pm$  0.5% in degassed MeOH, indicating some self-quenching of the platinum dyes in the core of the aggregate. Self-quenching by Pt-Pt interactions can be further confirmed by shorter lifetimes of the dye in poly b-1 compared to 3, namely,  $14 \pm 1 \,\mu s$  in degassed solution (Table 2). However, aggregation in **poly b-2** was considerably more pronounced, as evidenced by particularly low PLQYs in MeOH and low PLQYs in CHCl<sub>3</sub>, not exceeding  $1.1 \pm 0.5 \,\mu s$  in the latter case. It is to note that the influence of the solvent (MeOH vs CHCl<sub>3</sub>) on the values for PLQY and lifetimes cannot be retrieved directly from these experiments since 3 is not soluble in MeOH. However, these results indicate a significant suppression of self-quenching of the platinum chromophores when copolymerized with the carbazole dye like in **poly b-1**.

To further investigate the characteristics of the energy transfer in the host/guest system, a blend of **poly b-2** and **poly b-3** was prepared, using the same molar ratio (3:6 = 3:17) as in the

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block random copolymer poly b-1. poly b-2 and poly b-3 were mixed in CHCl<sub>3</sub>, and the solvent was evaporated. The dried residue was dispersed in methanol (0.1 wt %), resulting in the formation of aggregates with a diameter of 90 nm (PDI = 0.10). Luminescence measurements revealed an emission maximum of 475 nm in MeOH ( $\lambda_{ex} = 360$  nm), which is comparable to the emission maximum of 483 nm for **poly b-3** ( $\lambda_{ex} = 360$  nm) (vide infra). Excitation of poly b-2/poly b-3 in methanol at 460 nm revealed weak emission with maxima at 577 and 680 nm, which are comparable to the emission maxima of **poly b-2** in methanol ( $\lambda_{ex} = 470$  nm) located at 586 and 708 nm. Although both host and guest should be in close proximity in the core of the aggregate, no energy transfer occurred. The same accounts for photoluminescence thin film spectra of the polymer blend poly b-2/poly b-3, which were obtained by drop-casting either a MeOH solution or a CHCl<sub>3</sub> solution, containing 1 mg mL<sup>-1</sup> of the polymer blend, onto a glass slide. Excitation of the obtained film (either from MeOH or from CHCl<sub>3</sub>) at 360 nm revealed mainly blue emission at 434 nm and almost no red emission at 615 nm (see Supporting Information).

According to these results, it is essential to copolymerize host and guest in order to provide an efficient energy transfer when exciting the material at 360 nm. Simple blending of a carbazole host bearing copolymer with a platinum guest bearing copolymer, on the contrary, does not result in the desired energy transfer. Thus, a critical distance of platinum guest and carbazole host has to be maintained to guarantee efficient energy transfer. According to Förster theory, an estimated radius for which 50% of the populated excited states of the host are transferred to the guest is about 4 nm.<sup>32,33</sup> In the case of **poly b-1**, the highest possible intramacromolecular distance of two chromophores was estimated using an MM2 optimized model to be about 5 nm. Thus, at least some energy transfer should even occur in a solution of **poly b-1** in a nonselective solvent. This inconsistency and all observations reported above might be best explained by the formation of carbazole-platinum complex aggregates under solid state conditions (like in thin films or micelle cores) and eventually exciplex emission from these aggregates. In a good solvent for the carbazole moiety, these aggregates are broken and platinum complex self-aggregation occurs. The resulting platinum complex excimer emission is very weak and hardly observable. Although no direct spectroscopic evidence for this hypothesis could be retrieved, further experiments support this theory.

First, the luminescence spectrum of **poly b-1** in CHCl<sub>3</sub> at 77 K exhibited the blue emission of the host and the red emission of the guest complex with its maximum at 606 nm ( $\lambda_{ex} = 370$  nm, cf. Supporting Information). The blue shift of the emission maximum of the platinum dye can be attributed to rigidochromic effects.<sup>41</sup> More importantly, the experiment clearly reveals the feasibility of energy transfer in solution. Presumably, thermal deactivation of the platinum dye is the reason for the absence of platinum luminescence at room temperature in nonselective solvents.

Second, the originally red-emitting MeOH dispersion of **poly b-1** ( $\lambda_{max} = 628 \text{ nm}$ ; [**poly b-1**] =  $1.0 \times 10^{-1} \text{ mg/mL}$ ; 1 mL) instantly turned green upon addition of CH<sub>2</sub>Cl<sub>2</sub> (1 mL), characterized by a broad emission band at 504 nm (Figure 6). DLS measurements confirmed the presence of triblock random copolymer aggregates with a diameter of about 300 nm under these conditions. The increase of aggregate diameter can be explained by swelling of the aggregate due to increased incorporation of solvent into the aggregate's core. In fact, not



Figure 5. Emission spectra of **poly b-1** ( $\Box$ ) ( $\lambda_{ex} = 370$  nm) and **poly b-2** ( $\Delta$ ) ( $\lambda_{ex} = 470$  nm) measured in degassed MeOH at room temperature ([**poly b-1**] =  $1.0 \times 10^{-1}$  mg/mL, [**poly b-2**] =  $1.4 \times 10^{-1}$  mg/mL). The luminescence intensity of the broad excimer emission of **poly b-2** in MeOH ( $\bigcirc$ ) is about 20 times lower compared to the luminescence intensity of **poly b-1** in MeOH at 628 nm.



**Figure 6.** Emission spectra of **poly b-1** measured in MeOH ( $\Box$ ) ([**poly b-1**] = 1.0 × 10<sup>-1</sup> mg/mL) and in MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 1:1 ( $\Delta$ ) ( $\lambda_{ex}$  = 370 nm in both cases).

only CH<sub>2</sub>Cl<sub>2</sub> but also MeOH were attained into the core, as revealed by the red-shifted emission wavelength<sup>42</sup> of the solvatochromic carbazole dye (cf. Supporting Information).<sup>43</sup>The solvatochromism of the carbazole dye shows that also the polarity

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<sup>(42)</sup> Investigating the solvatochromic emission behavior of the carbazole dye in the corresponding block copolymer system of **poly-b-3** revealed different emission maxima in the solvents MeOH ( $\lambda_{max} = 483$  nm), CHCl<sub>3</sub> ( $\lambda_{max} = 451$  nm), CH<sub>2</sub>Cl<sub>2</sub> ( $\lambda_{max} = 459$  nm), and MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 1:1 ( $\lambda_{max} = 504$  nm). Similar maxima were obtained for the corresponding monomer **6** (cf. Supporting Information). At present, a reasonable explanation is missing for the surprisingly low energy of the emission maximum in MeOH/CH<sub>2</sub>Cl<sub>2</sub>. Effects such as aggregation and excimer formation cannot be excluded as the reason for this behavior, especially because carbazole derivatives are well known to form excimers.<sup>43</sup>

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of the host/guest environment plays a significant role for the energy transfer efficiency. The emission energy of the donor can be affected by the solvent polarity, which in addition leads to a different spectral overlap with the acceptor absorption band.

The latter experiment constitutes a proof of principle for using such aggregates for sensing purposes and further supports the hypothesis that carbazole—platinum complex exciplexes are responsible for the red emission in the solid state and in polymer aggregates.

## Conclusion

In this contribution, the synthesis, characterization, and selfassembly of amphiphilic triblock random copolymers bearing a blue fluorescent host and a red phosphorescent guest prepared by ROMP were presented. Emission properties of the amphiphilic triblock random copolymer dissolved in a nonselective solvent are exclusively determined by the host material. Only the blue emission of the carbazole derivative can be observed. When the polymer is dissolved in a selective solvent, polymer aggregates are formed and energy transfer occurs. In this case deep red phosphorescence stemming from the platinum complex used as guest component can be observed. The amphiphilic triblock random copolymer architecture, thus, allows for (a) the dispersion of the platinum chromophore in a solvent in which the parent chromophore is insoluble, (b) the realization of a large Stokes shift of about 260 nm, and (c) significant suppression of platinum complex self-aggregation, resulting in considerable phosphorescent quantum yields. Addition of an unselective solvent to the polymer aggregates dispersed in a selective solvent leads to the virtual shutdown of the energy transfer and recovery of the host emission.

The effect is attributed not only to fluorescence resonance energy transfer, i.e., change of distance of the chromophores, but also to the formation of dye aggregates. In the absence of a good solvent for the carbazole moiety, carbazole–platinum complex aggregates are formed in the core of the block copolymer micelle. These host–guest aggregates are responsible for an efficient energy transfer, and the corresponding exciplex type exhibits a good phosphorescence quantum yield. Furthermore, platinum complex self-aggregation is suppressed by physical separation.<sup>44</sup> Such undesired self-aggregation resulting in almost nonluminescent excimers of the platinum complexes was observed in block copolymer aggregates without copolymerized carbazole host.

The amphiphilic triblock random copolymers introduced herein hold promise for applications in optical sensing. Investigations along this line are currently ongoing in our laboratories.

## **Experimental Section**

Manipulations were performed under an inert atmosphere of purified nitrogen or argon using Schlenk techniques and/or a glovebox. Unless otherwise noted, materials were obtained from commercial sources (Aldrich, Fluka, or Lancaster) and were used without further purification. 5-Formyl-8-hydroxyquinoline<sup>24</sup> and the initiator (H<sub>2</sub>IMes)(pyridine)<sub>2</sub>RuCl<sub>2</sub>(=CHPh) (**G**)<sup>45a</sup> were prepared according to the literature. <sup>1</sup>H NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer at 500 MHz; <sup>13</sup>C(<sup>1</sup>H) NMR spectra were recorded at 125 MHz. Assignment of the peaks was done by DEPT and COSY NMR spectroscopy. Solvent residual peaks were used for referencing the NMR spectra to the corresponding values given in the literature.<sup>46</sup> FT-IR spectra were obtained from films on KBr or NaCl windows with a Perkin-Elmer Spectrum One and a DTGS detector. UV-visible absorption spectra were recorded on a Cary 50 Bio UV-visible spectrophotometer; fluorescence spectra, on a Hitachi F-7000 fluorescence spectrometer (www.inula.at) equipped with a red-sensitive photomultiplier R 928 from Hamamatsu (www.hamamatsu.com). The emission spectra were not corrected for the sensitivity of the PMT. Phase angle measurements in solution were performed using the following system. A dual-phase lock-in amplifier (DSP 830; Stanford Research Inc.) was used for sine-wave modulation of the LED at a frequency of 5.5 kHz and for detection. The optical system consisted of a blue LED ( $\lambda_{max} = 470$  nm, Roithner Lasertechnik; Vienna, Austria) combined with a BG 12 band-pass filter (Schott; Mainz, Germany) and a red-sensitive PMT module (H5701-02; Hamamatsu; Herrsching, Germany) equipped with a long-pass filter (OG590; Schott; Mainz, Germany). The measurements were carried out in aerated and in degassed MeOH and CHCl3 solutions. The apparent lifetimes were determined according to the equation  $\tan \Delta \phi = 2\pi \nu \tau$ , where  $\Delta \phi$  indicates the phase shift,  $\nu$  the modulation frequency, and  $\tau$ the luminescence lifetime. Photoluminescence (PL) quantum yields were measured on a Hitachi F-7000 fluorescence spectrometer (www.inula.at) equipped with a red-sensitive photomultiplier R 928 from Hamamatsu (www.hamamatsu.com) and a Perkin-Elmer Lambda 9 UV/vis/near-infrared spectrophotometer. The emission spectra were not corrected for the sensitivity of the PMT. Relative quantum yield of luminescence was determined according Demas and Crosby<sup>47</sup> using 4-dicyanomethylene-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyrane ( $\Phi = 0.57$ )<sup>38</sup> as a standard. DSC measurements were made with a Perkin-Elmer Pyris Diamond differential scanning calorimeter equipped with a Perkin-Elmer CCA7 cooling system using liquid nitrogen. A nitrogen flow of 20 mL/min and a heating rate of 10 °C/min were used. Glass transition temperatures  $(T_g)$  from the second heating run were read as the midpoint of change in heat capacity. The number average molecular weights  $(M_n)$  as well as the polydispersity index (PDI) were determined by gel permeation chromatography with THF and CHCl3 as solvent using the following arrangements. THF setup: Merck Hitachi L6000 pump, separation columns of Polymer Standards Service, 8 × 300 mm SDV 5  $\mu$ m grade size (106, 104, and 103 Å), combined refractive index-viscosity detector from Viscotec, Viscotec 200. CHCl<sub>3</sub> setup: Merck Hitachi L6000 pump, separation columns of Polymer Standards Service, 8  $\times$  300 mm SDV linear XL 5  $\mu$ m grade size, differential refractometer 410 detector from Waters Ltd. Polystyrene standards purchased from Polymer Standard Service were used for calibration of both setups. Particle sizes were determined by DLS using the Malvern ZetaSizer NanoZS equipped with a 633 nm laser. Measurements were performed at 20 °C. MALDI-TOF mass spectra were recorded on a Micromass TofSpec 2E. The instrument is equipped with a nitrogen laser (337 nm wavelength, operated at a frequency of 5 Hz) and a time lag focusing unit. Spectra were taken in reflectron mode at an accelerating voltage of +20 kV. Analysis of data was done with MassLynx 3.4 (Micromass, Manchester, UK). Samples were dissolved in THF (1 mg/mL). Dithranol or retinoic acid was used as matrix (10 mg/mL in THF). Solutions were mixed in the cap of a microtube in the ratio of 1  $\mu$ L:10  $\mu$ L. A 0.5  $\mu$ L amount of the resulting mixture was spotted onto the target and air-dried.

Synthesis of the Polymerizable Pt(II) Complex 3. To a solution of cyclopentadiene (150  $\mu$ L, 1.82 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (6 mL) was added dropwise acryloyl chloride (25  $\mu$ L, 0.31 mmol). The

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yellow reaction mixture was stirred at room temperature. After 3 h **2** (105.9 mg; 0.150 mmol), pyridine (20  $\mu$ L; 0.248 mmol), and DMAP (1.9 mg; 0.016 mmol; 10.4 mol %) were added, and the orange solution was stirred at room temperature. After 20 h the solvent was removed and the orange residue was purified by column chromatography (SiO<sub>2</sub>, eluent Cy/EA = 2:1, Cy/EA = 1:2 and EA;  $R_f = 0.2$  in Cy/EA = 2:1). The resulting orange solid was further purified by washing with hot methanol and n-pentane. Yield: 20.0 mg (16%). Mixture of 67% endo- and 33% exo-derivatives; only NMR data for the *endo*-isomer are given. <sup>1</sup>H NMR ( $\delta$ , 20 °C, CDCl<sub>3</sub>, 500 MHz): 9.97 (s, 1H, *CHO*), 9.88 (d, 1H,  ${}^{3}J_{HH} = 8.5$  Hz, q<sup>4</sup>), 9.08 (d, 1H,  ${}^{3}J_{HH} = 4.9$  Hz, q<sup>2</sup>), 8.94 (d, 1H,  ${}^{3}J_{HH} = 5.6$  Hz, py<sup>6</sup>), 8.27 (d, 1H,  ${}^{3}J_{HH} = 7.8$  Hz, ph<sup>6</sup>), 7.86 (d, 1H,  ${}^{3}J_{HH} = 8.3$  Hz,  $q^{6}$ ), 7.54–7.52 (m, 1H,  $q^{3}$ ), 7.37 (d, 1H,  ${}^{3}J_{HH} = 7.3$  Hz, py<sup>4</sup>), 7.28 (d, 1H,  ${}^{3}J_{HH} = 8.3$  Hz, ph<sup>3</sup>), 7.19 (t, 1H,  ${}^{3}J_{HH} = 7.1$  Hz, py<sup>5</sup>), 7.11 (t, 1H,  ${}^{3}J_{HH} = 7.6$  Hz, ph<sup>4</sup>), 7.02–6.99 (m, 1H, ph<sup>5</sup>), 6.95 (d, 1H,  ${}^{3}J_{HH} = 8.3$  Hz, q<sup>7</sup>), 6.19–6.18 (m, 1H, nb<sup>5</sup>), 5.93–5.91 (m, 1H, nb<sup>6</sup>), 4.10 (t, 2H,  ${}^{3}J_{HH} = 6.6$  Hz, CH<sub>2</sub><sup>1</sup>), 4.04–3.97 (m, 2H, CH<sub>2</sub><sup>11</sup>), 3.20 (bs, 1H, nb1), 2.96-2.93 (m, 1H, nb2), 2.90 (bs, 1H, nb4), 2.00-1.87 (m, 4H, nb<sup>3,7</sup>), 1.64-1.51 (m, 6H, CH<sub>2</sub><sup>2-4</sup>), 1.43-1.26 (m, 12H, CH2<sup>5-10</sup>). <sup>13</sup>C(<sup>1</sup>H) NMR (δ, 20 °C, CDCl<sub>3</sub>, 125 MHz): 190.4 (1C, CHO), 175.0 (1C, C=O), 174.0 (1C, q<sup>8</sup>), 156.1 (1C, py<sup>3</sup>), 153.1 (1C, ph<sup>2</sup>), 148.3 (1C, py<sup>6</sup>), 147.0, 146.9 (2C, py<sup>2</sup>, q<sup>8a</sup>), 143.2 (1C, q<sup>2</sup>), 141.4 (1C, ph<sup>3</sup>), 138.5 (1C, ph<sup>1</sup>), 137.9 (1C, nb<sup>5</sup>), 137.2 (1C, py<sup>4</sup>), 132.5 (1C, nb<sup>6</sup>), 131.3 (1C, q<sup>4</sup>), 130.4 (1C, q<sup>4</sup>a), 128.60, 128.59 (2C, ph<sup>6</sup>, q<sup>6</sup>), 124.1, 123.6 (2C, q<sup>3</sup>, ph<sup>5</sup>), 121.5, 121.4 (2C, ph<sup>4</sup>, py<sup>5</sup>), 117.3 (1C, q<sup>5</sup>), 115.1 (1C, q<sup>7</sup>), 69.4 (1C, CH<sub>2</sub><sup>1</sup>), 64.5 (1C, CH<sub>2</sub><sup>11</sup>), 49.8 (1C, nb<sup>7</sup>), 45.9 (1C, nb<sup>1</sup>), 43.5, 42.7 (2C, nb<sup>2,4</sup>), 29.7, 29.64, 29.62, 29.5, 29.4, 29.3, 29.1, 28.8, 26.3, 26.1 (10C, nb<sup>3</sup>, CH<sub>2</sub><sup>2-10</sup>). Characteristic *exo*-signals: 176.5 (C=O), 138.2, 135.9 (nb<sup>5,6</sup>), 64.7 (COOCH<sub>2</sub>). IR (film on NaCl window cast from CHCl<sub>3</sub> solution, cm<sup>-1</sup>): 3093 (w), 3060 (w), 2926 (m), 2852 (m), 2709 (w), 1729 (m), 1663 (m), 1588 (m), 1561 (m), 1506 (s), 1472 (m), 1427 (m), 1396 (w), 1365 (w), 1342 (m), 1309 (w), 1276 (m), 1245 (m), 1210 (m), 1185 (w), 1172 (w), 1147 (m), 1111 (w), 1063 (w), 1027 (w), 840 (w), 828 (w), 790 (w), 782 (w), 733 (m), 714 (w), 650 (m), 598 (w). Anal. Found for C<sub>40</sub>H<sub>44</sub>N<sub>2</sub>O<sub>5</sub>Pt: C, 57.89; H, 5.55; N, 3.18. Calcd: C, 58.03; H, 5.36; N, 3.38. MALDI-TOF MS: calcd 850.28; found 850.28.

Synthesis of Bicyclo[2.2.1]hept-5-ene-2-carboxylicacid 11-[3,6-Di(4-formylphenyl)carbazol-9-yl]undecyl Ester (mixture of the endo- and exo-form) (6). Cyclopentadiene (62.2  $\mu$ L, 0.76 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (3 mL). Acryloyl chloride (18.4  $\mu$ L, 0.23 mmol) was added dropwise to the reaction mixture, and the solution was stirred at room temperature for 7 h. Subsequently 5 (103 mg, 0.19 mmol) and DMAP (2 mg, 0.02 mmol) were added. The reaction mixture was cooled using an ice bath, and pyridine  $(20 \ \mu L, 0.25 \ mmol)$  was added slowly. The reaction was stirred for a further 30 min. Then, the ice bath was removed and the mixture was stirred at room temperature for 24 h. The reaction was quenched with H<sub>2</sub>O (2 mL). Then, the organic layer was washed four times with saturated NaHCO3 solution (50 mL) and four times with 5% HCl solution (50 mL). After drying the organic layer over Na<sub>2</sub>SO<sub>4</sub> and removing the solvent under vacuum the residue was purified by column chromatography on silica (Cy/EA = 15:1;  $R_f$  = 0.86 in Cy/EA = 1:1) to give a yellow solid (70 mg, 56%). Mixture of 78% endo- and 22% exo-derivatives; only NMR data for the *endo*-isomer are given. <sup>1</sup>H NMR ( $\delta$ , 20 °C, CDCl<sub>3</sub>, 500 MHz): 10.08 (s, 2H, CHO), 8.45 (s, 2H, c<sup>4,5</sup>), 8.01-7.99 (d, 4H,  ${}^{3}J_{HH} = 8.3$  Hz, ph<sup>3,5</sup>), 7.92–7.90 (d, 4H,  ${}^{3}J_{HH} = 8.3$  Hz, ph<sup>2,6</sup>), 7.82–7.80 (d, 2H,  ${}^{3}J_{HH} = 8.5$  Hz,  $c^{2,7}$ ), 7.54–7.53 (d, 2H,  ${}^{3}J_{HH} =$ 8.5 Hz, c<sup>1,8</sup>), 6.19-6.17 (bs, 1H, nb<sup>5</sup>), 5.92-5.90 (bs, 1H, nb<sup>6</sup>), 4.39-4.37 (t, 2H, undec1), 4.07-3.98 (m, 2H, undec11), 3.19 (s, 1H, nb<sup>1</sup>), 2.95-2.89 (m, 2H, nb<sup>2,4</sup>), 1.96-1.86 (m, 3H, nb<sup>3</sup>, undec<sup>2</sup>), 1.61-1.50 (m, 5H, nb<sup>3</sup>, nb<sup>7</sup>, undec<sup>10</sup>), 1.37-1.25 (m, 14H, undec<sup>3-9</sup>). Characteristic *exo* signals: 6.14–6.09 (m, 2H, nb<sup>5,6</sup>). <sup>13</sup>C(<sup>1</sup>H) NMR (δ, 20 °C, CDCl<sub>3</sub>, 125 MHz): 191.9 (2C, *CHO*), 174.7 (1C, nbCOO), 147.8 (2C, ph<sup>1</sup>), 141.0 (2C, c<sup>3,6</sup>), 137.6 (1C, nb<sup>5</sup>), 135.6 (1C, nb<sup>6</sup>), 134.4, 132.2 (4C, c<sup>8a,9a</sup>, ph<sup>4</sup>), 130.3 (4C, ph<sup>3,5</sup>), 127.4 (4C, ph<sup>2,6</sup>), 125.5 (2C, c<sup>4,5</sup>), 123.4 (2C, c<sup>4a,4b</sup>), 119.3 (2C, c<sup>2,7</sup>), 109.4 (2C, c<sup>1,8</sup>), 64.2 (1C, undec<sup>11</sup>), 49.6 (1C, nb<sup>7</sup>), 45.6 (1C, nb<sup>1</sup>), 43.4 (1C, undec<sup>1</sup>), 43.2, 42.4 (2C, nb<sup>2,4</sup>), 31.8 (1C, undec<sup>10</sup>), 29.6–29.0 (5C, undec<sup>4–8</sup>), 28.5 (1C, undec<sup>2</sup>), 27.2 (1C, undec<sup>3</sup>), 25.8 (2C, undec<sup>9</sup>, nb<sup>3</sup>). Characteristic *exo*-signals: 176.2 (1C, nbCOO), 137.8 (2C, nb<sup>5,6</sup>). IR (film on KBr window cast from CH<sub>2</sub>Cl<sub>2</sub> solution, cm<sup>-1</sup>): 2925 (s), 2854 (s), 2730 (w), 1727 (m), 1698 (s), 1631 (w), 1594 (s), 1564 (w), 1518 (w), 1483 (s), 1465 (m), 1391 (w), 1353 (w), 1335 (w), 1308 (w), 1272 (w), 1215 (m), 1171 (m), 1028 (w), 905 (w), 838 (w), 804 (m), 719 (w). Anal. Found for C<sub>33</sub>H<sub>39</sub>NO<sub>4</sub>: C,77.00; H, 7.88; N, 2.89. Calcd: C, 77.16; H, 7.65; N, 2.73.

Synthesis of poly b-1.8 (70 mg, 0.13 mmol) was dissolved in dry, degassed CH<sub>2</sub>Cl<sub>2</sub> (5 mL). Then, the reaction mixture was concentrated by removing approximately 1 mL of the solvent in vacuo. A solution of the initiator G (1.0 mg, 0.0014 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was added to the reaction mixture, which was stirred at room temperature for 2 h. TLC monitoring revealed completeness of the reaction by the absence of the monomer spot (TLC for 8: EA; detection: 2% KMnO<sub>4</sub> solution,  $R_f = 0.5$ ). Then, 7 (58 mg, 0.27 mmol) was added. The reaction mixture was stirred for 1 h until the absence of the monomer was confirmed by TLC (Cy:EA = 5:1; detection: 2% KMnO<sub>4</sub> solution;  $R_f = 0.6$ ). Finally, a mixture of 3 (3.4 mg, 0.0041 mmol) and 6 (15.6 mg, 0.023 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was added to the reaction mixture. After 1 h the absence of both monomers was confirmed by TLC (Cy:EA =1:1, UV/vis detection;  $R_f \mathbf{3} = 0.6$ ,  $R_f \mathbf{6} = 0.8$ ). The polymerization reaction was quenched by adding ethyl vinyl ether (50  $\mu$ L). After stirring for another 15 min the reaction mixture was concentrated by partially removing the solvent under reduced pressure. Finally, the reaction mixture was added dropwise to stirred n-pentane (80 mL) to precipitate the polymer. Purification was done by subsequent repeated precipitation (2 times) of CH<sub>2</sub>Cl<sub>2</sub> solutions from *n*-pentane. The polymer was dried in vacuo. Yield: 93 mg (63%). <sup>1</sup>H NMR ( $\delta$ , 20 °C, CDCl<sub>3</sub>, 500 MHz): 10.01 (bs, ≈0.05H, *CHO*), 8.36 (bs,  $\approx 0.09$ H, c<sup>4,5</sup>), 8.05-7.63 (m,  $\approx 0.32$ H, ph<sup>2,3,5,6</sup>, c<sup>2,7</sup>), 7.42 (bs, ≈0.09H, c<sup>1,8</sup>), 5.57–5.10 (m, 2H, HC=CH), 4.36–4.02 (m, 1.2H, COOCH<sub>2</sub>), 3.80-3.45 (m, 11H, OCH<sub>2</sub>, OCH<sub>3</sub>), 3.39-2.62 (m, 4H, cp<sup>1-3,5</sup>), 1.97 (bs, 1H, cp<sup>4a</sup>), 1.47 (bs, 1H, cp<sup>4b</sup>), 1.20 (t, 2H, OCH<sub>2</sub>CH<sub>3</sub>). FT-IR (film on NaCl, cm<sup>-1</sup>): 3621 (w), 3450 (w), 2952 (m), 2868 (m), 1732 (s), 1599 (w), 1437 (m), 1383 (w), 1349 (w), 1256 (m), 1196 (m), 1172 (s), 1113 (m), 1045 (w), 965 (w,  $\nu_{\text{trans C=C}}$ , 842 (w), 803 (w), 742 (w,  $\nu_{\text{cis C=C}}$ ). GPC (in THF):  $M_n$ 75 100 g/mol; PDI 1.53. GPC (in CHCl<sub>3</sub>): M<sub>n</sub> 92 300 g/mol, PDI 1.59. DSC:  $T_{\rm g}$  not observed.

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**Supporting Information Available:** Detailed synthetic procedures, comprehensive photophysical data (tables, absorption, emission and excitation spectra), DLS, and MALDI-TOF data. This material is available free of charge via the Internet at http://pubs.acs.org.

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