

# Construction of phthalocyanine-terminated polystyrene nanoarchitectures<sup>†</sup>

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**Nanostructuring of phthalocyanine-based materials is a powerful tool towards the preparation of new materials with outstanding properties. It has been previously shown that porphyrin-functionalized and phthalocyanine-functionalized polymers give rise to nanosized aggregates. With the goal in mind of searching new phthalocyanine-containing polymeric materials that are able to self-organize into stable supramolecular nanostructures, we have prepared unsymmetrically functionalized Zn(II) phthalocyanines that are able to behave as initiators in the atom transfer radical polymerization of styrene. Hybrid phthalocyanine-polystyrene materials of different tail lengths have been prepared, and their self-organization behavior was studied by means of UV-Vis spectroscopy and transmission electron microscopy. Copyright © 2012 John Wiley & Sons, Ltd.**

**Keywords:** ATRP polymerization; nanoaggregates; phthalocyanines

## INTRODUCTION

The controlled organization of functional molecules into self-assembled arrays is an active area of research in chemistry and nanoscience. Following a bottom-up approach, well-defined nanoscale objects with improved photophysical and (opto) electronic properties can be obtained. To achieve this goal, the molecules have to be programmed for self-organizing through a highly efficient cooperation between the units.

Phthalocyanines (Pcs) are well-known 18- $\pi$ -electron aromatic molecules with unique physicochemical properties that make them interesting building blocks to be used in different fields of science and technology, such as photovoltaics, sensing, liquid crystals, and field-effect transistors.<sup>[1–4]</sup> The inherent  $\pi$ - $\pi$  stacking abilities of Pcs make it possible to obtain supramolecular structures, but some structural modifications at the periphery of Pc rings may improve their inherent self-organization properties.<sup>[5–10]</sup> A wide range of interactions have been used as tools to organize Pc-based systems in solution such as hydrogen bonding,<sup>[11]</sup> donor-acceptor,<sup>[12]</sup> and metal-ligand interactions.<sup>[13,14]</sup> Many approaches have been explored for inducing the organization of functional molecules into condensed phases for their practical application in functional devices, such as liquid crystal<sup>[15–18]</sup> or thin film formation.<sup>[19,20]</sup> Amphiphilic Pcs have shown to assemble in Langmuir-Blodgett thin films<sup>[21–27]</sup> and also give rise to interesting architectures in solution.<sup>[28]</sup>

Phthalocyanines have also been integrated into polymeric networks as a way to obtain new materials with improved properties.<sup>[29–34]</sup> Pcs can be incorporated into macromolecular structures as side group, in the main chain and in a polymeric network. There are also a few reported examples of polymers containing a terminal Pc core. In particular, Kimura *et al.* reported the formation of polyacrylate-based amphiphilic Pcs through controlled living radical polymerization from a Pc-containing initiator, which self-assembled in solution into fibrous aggregates.<sup>[35]</sup> Within the living polymerization methods, atom transfer radical polymerization (ATRP) is a practical method for preparing well-defined polymers with a narrow molecular weight distribution ( $1.0 < M_w/M_n < 1.5$ ).<sup>[36]</sup>

In this paper, we describe the synthesis of amphiphilic Pc-terminated polymers through ATRP polymerization of styrene from a Pc-functionalized initiator and the study of its self-organizing properties in solution. Our aim is to gain stability in the aggregates that would stem from the polymeric nature of the hybrid and also to control the organization features of the material as a function of the polymer chain length, which can be controlled by the use of ATRP conditions.

## RESULTS AND DISCUSSION

The preparation of Pc-terminated copolymers requires adequately functionalized Pcs to be synthesized. The introduction of a hydroxy moiety at the Pc core seems appropriate to perform an esterification reaction with a typical halogenated ATRP initiator, such as 2-bromoisobutryl bromide. Therefore, an unsymmetrically

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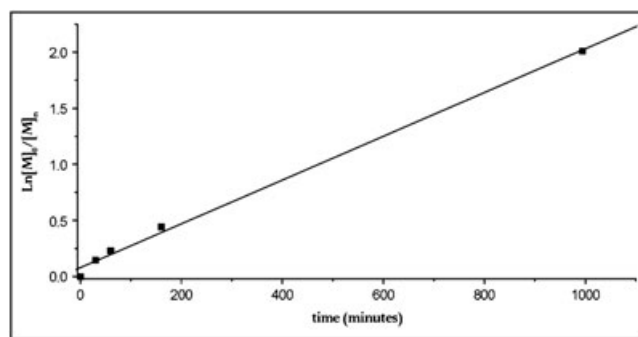
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substituted Zn(II)Pc having three isoindoles attached to solubilizing *tert*-butylphenoxy moieties and one isoindole functionalized with one 2-hydroxyethoxy moiety (**1**) has been prepared (Scheme 1) by statistical condensation of 4,5-di-*tert*-butylphenoxyphthalonitrile<sup>[37]</sup> and 4-(2-hydroxyethoxy)phthalonitrile<sup>[38]</sup> in the presence of lithium and pentanol to give metal-free Pc **2**, which was further metallated with Zn(OAc)<sub>2</sub>. This procedure, that is, the formation of the metal-free macrocycle and subsequent metallation, allows the use of unprotected 4-(2-hydroxyethoxy) phthalonitrile. However, further metallation of the macrocycle is compulsory to avoid undesired metallation processes during subsequent Cu(I)-catalyzed polymerization of the Pc initiator.<sup>[39]</sup> The resulting Zn(II)Pc **1** was reacted with a small excess of bromoisobutryl bromide in dry dichloromethane to give the Zn(II)Pc initiator **3** in 87% yield. All Pc derivatives were characterized by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF), nuclear magnetic resonance (NMR), and UV-Vis.

Bulk polymerization of styrene under ATRP conditions was performed with Zn(II)Pc initiator **3** (Scheme 1). Copper(I) bromide was used as the catalyst with two equivalents of pentamethyl diethylene triamine as the ligand for the copper ion. The polymerizations were performed at 90 °C in a mixture of styrene/anisole (2/1, v/v). The conversion of styrene during the polymerization was monitored by gas chromatography (GC) with anisole as the internal standard.

Figure 1 shows the semilogarithmic plot of  $\ln[M]_0/[M]_n$  versus the reaction time for the polymerization reaction. The linear relation indicates that the polymerization follows first-order kinetics, and therefore, it likely proceeds in a controlled fashion. Zn(II)Pc-polystyrenes **4a** and **4b** with two different polystyrene tail lengths were prepared (Table 1) by terminating the two separate polymerizations at different degrees of styrene conversion. Gel permeation chromatography (GPC) studies of as-prepared polymer **4a** revealed the presence of a small amount of a low molecular weight compound with a strong absorbance at  $\lambda = 684$  nm (i.e., Pc Q-band region) before purification by size exclusion chromatography (SEC). The compound was separated

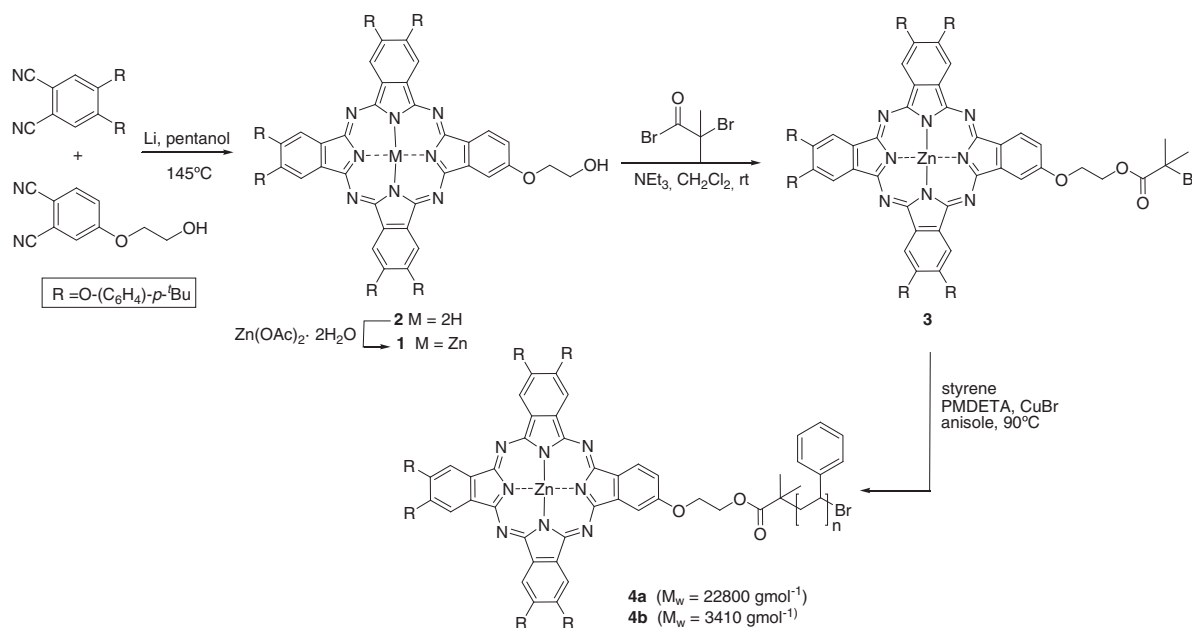


**Figure 1.** Semilogarithmic plot of  $\ln[M]_0/[M]_n$  versus reaction time for the polymerization of styrene from Zn(II)Pc initiator **3**

from the polymer and analyzed by MALDI-TOF spectrometry. It proved to be a compound twice the mass of the Zn(II)Pc unit, plus two or three styrene units, pointing to the termination of two radical species in the beginning of the polymerization process. Because Pcs have the tendency to self-assemble, the early termination is probably promoted by a high local concentration of initiators. Furthermore, this effect is probably enhanced by the low solubility of Zn(II)Pc **3** in the reaction mixture of styrene and anisole. To avoid this early termination reaction, the polymerization in a subsequent experiment towards **4b** was performed at lower concentrations of the Zn(II)Pc initiator, that is, more diluted with styrene (2.5 times) because a lower concentration of radicals in solution would decrease the chance of termination. GPC analysis of crude **4b** showed no formation of low molecular weight compounds and, as expected, a decreased polydispersity because of the early termination of the polymerization reaction at a lower degree of styrene conversion.

Both reaction mixtures were purified by SEC (Biobeads, toluene), and the different polymer batches were analyzed by GPC (Table 1 and Fig. 2), MALDI-TOF mass spectrometry, and UV-Vis.

The GPC profiles (Fig. 2) of the Zn(II)Pc-polystyrene hybrids were measured at two different wavelengths:  $\lambda = 254$  nm



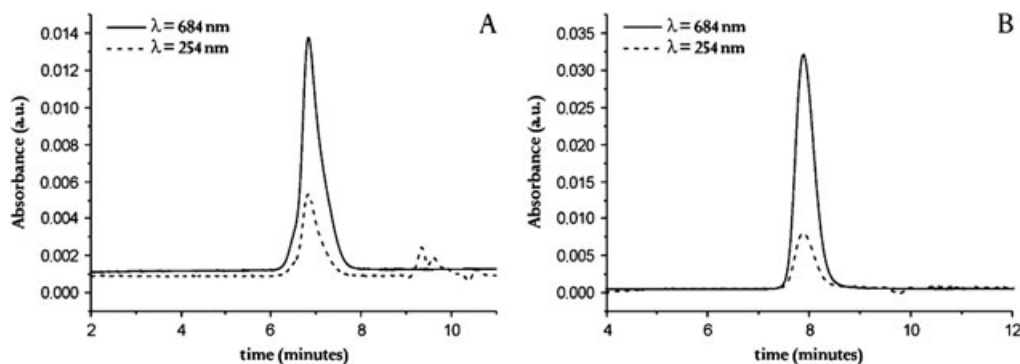
**Scheme 1.** Synthesis of Zn(II)Pc initiator **3** and subsequent atom transfer radical polymerization of styrene

**Table 1.** Polymerization conditions and characterization of Zn(II)Pc–polystyrene compounds

Polystyrene product	Polymerization conditions	PDI	$M_n^a$ (kg·mol <sup>-1</sup> )	$M_w^a$ (kg·mol <sup>-1</sup> )
<b>4a</b>	1 equiv. CuBr, 2 equiv. PMDETA	1.43	15.9	22.8
<b>4b</b>	1 equiv. CuBr, 2 equiv. PMDETA	1.21	2.80	3.41

Pc, phthalocyanine; PDI, polydispersity index; equiv., equivalent; PMDETA, pentamethyl diethylene triamine; GPC, gel permeation chromatography.

<sup>a</sup>Measured by GPC at  $\lambda = 254$  nm.



**Figure 2.** Gel permeation chromatography profiles of Zn(II)Pc–polystyrene **4a** (A) and **4b** (B), measured at two different wavelengths:  $\lambda = 684$  nm (solid lines) and  $\lambda = 254$  nm (dashed lines)

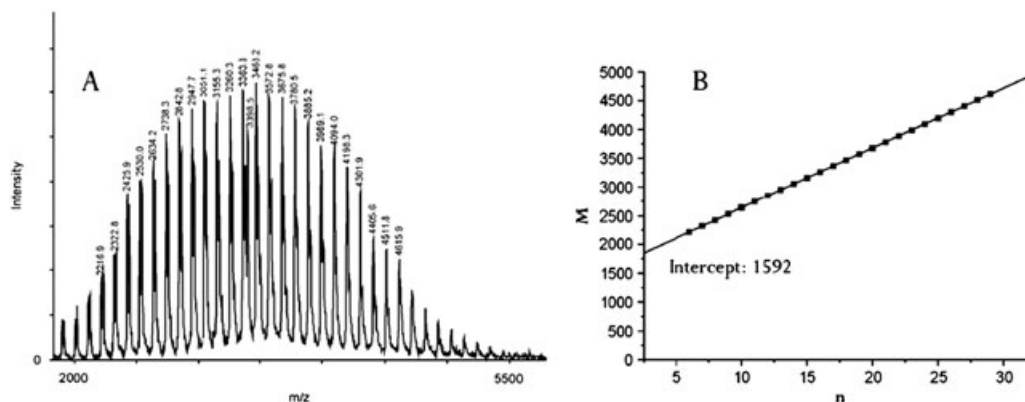
(polystyrene tail) and  $\lambda = 684$  nm (Pc Q-band region); both profiles show a good overlap, which indicates that polymers **4a** and **4b** contain the terminal Zn(II)Pc group.

MALDI-TOF spectra were recorded with dithranol as the matrix in linear mode. In Fig. 3A, the spectrum for Zn(II)Pc–polystyrene **4b** is shown. The MALDI-TOF spectrum revealed two sets of masses both with a regular interval of 104 *uma*, as expected for the styrene monomer unit. End-group analysis of the polystyrene hybrids was performed to identify the correct mass for the combined end groups. The plot of the most dominant mass set is shown in Fig. 3B. The intercept at the *y*-axis corresponds with the end group of the polymer. For this set of masses, the end groups have a combined mass of 1592 *uma*, which corresponds with a Zn(II)Pc moiety at one end and the absence of an end group at the other end of the polymer. The analysis of the second set of masses revealed a similar polymer with the Zn(II)Pc at one end and a hydroxyl functionality at the other end of the polymer. These two products are expected to be formed during

the work-up of the ATRP reaction mixture in the presence of water. A third mass set, much less pronounced than the other two, points to Zn(II)Pc–polystyrene systems that form supramolecular complexes with the matrix used for this measurement (dithranol, MW = 226 *uma*). The spectrum depicted in Fig. 3A also shows a prominent peak at  $m/z = 3398.5$ . This peak probably results from partial fragmentation during the MALDI-TOF measurement because of the high energy of the laser. The resulting Pc fragment is visible in the MALDI-TOF spectrum around  $m/z = 1600$ .

#### Aggregation behavior of Zn(II)Pc-terminated polystyrenes

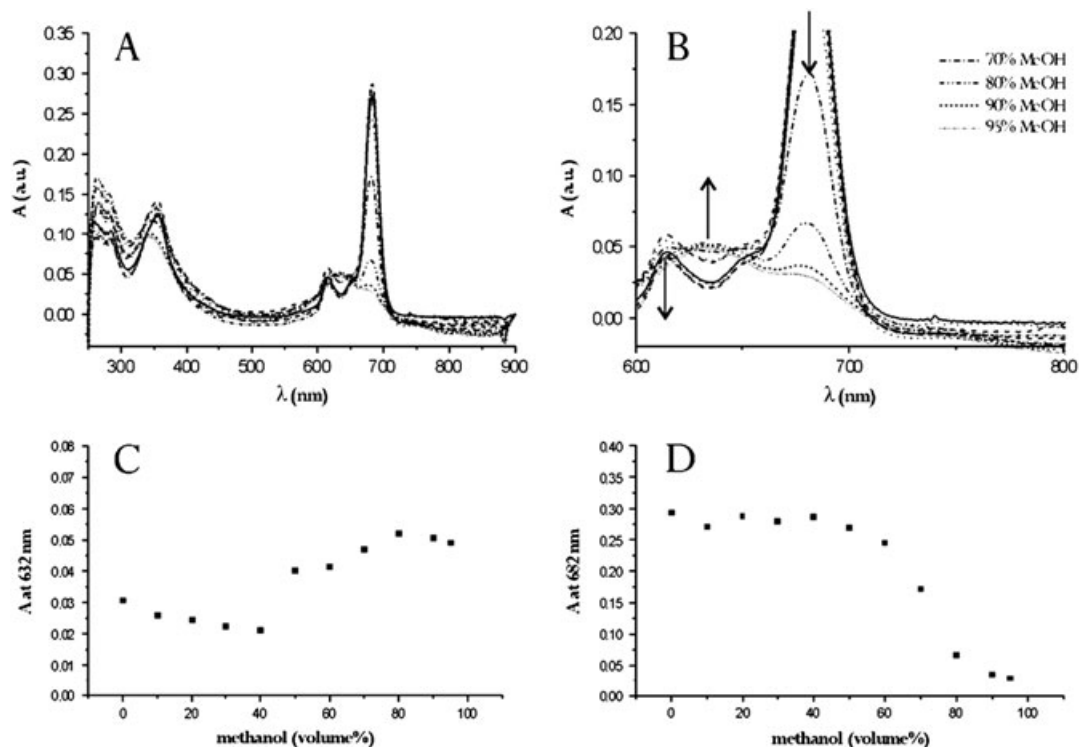
It is well-established that, in general, addition of polar solvents such as methanol into solutions of Pcs, for instance in chloroform, induces the formation of stacks.<sup>[9,10]</sup> UV–Vis studies have been performed to investigate the aggregation behavior of **4a** and **4b** in chloroform/methanol mixtures. The UV–Vis spectrum



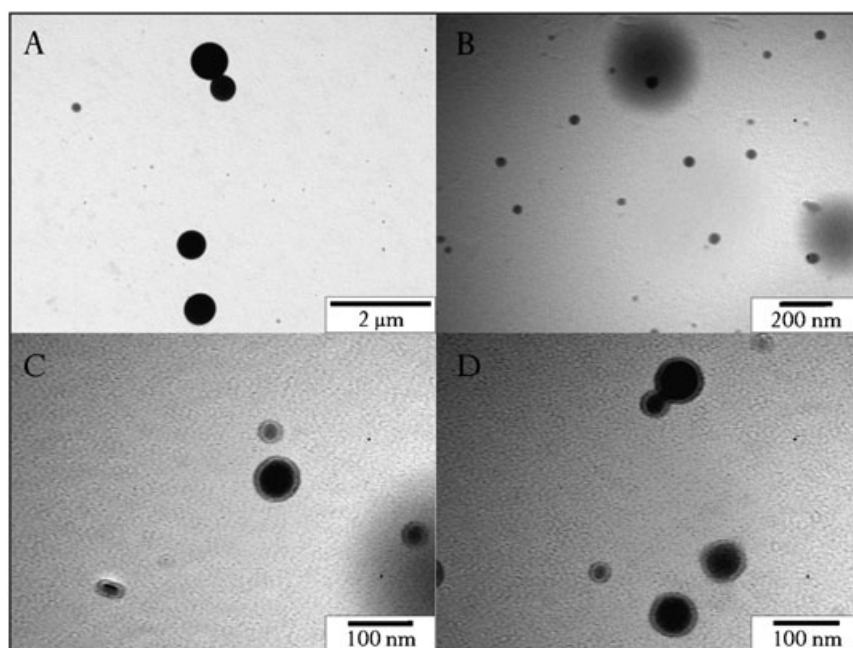
**Figure 3.** (A) Matrix-assisted laser desorption/ionization time-of-flight spectrum of Zn(II)Pc–polystyrene **4b** (linear mode). (B) Plot of the peak mass versus monomer units, with intercept at the *y*-axis of 1592

of **4b** in chloroform (Fig. 4A, solid line, concentration =  $10^{-5}$  M) shows a sharp peak in the Q-band region at 682 nm with a shoulder at 615 nm and a Soret band at 355 nm. Upon addition of increasing amounts of methanol (Fig. 4B, dashed lines), the Q-band started to broaden. At 50% (v/v) of methanol, the band at 682 nm sharply decreased, and a new band at 632 nm showed up (Fig. 4C and D). Further raising the methanol concentration

caused an increase of the band at 632 until a maximum was reached at 80% of methanol and a decrease of the band at 682 until it is nearly completely faded. The Soret band at 355 nm broadened and shifted to lower wavelengths at higher methanol concentrations. These spectral changes pointed to the stacking of the Pc units, as a result of the formation of aggregates by Zn(II)Pc–polystyrene hybrids **4a** and **4b**.



**Figure 4.** (A) and (B) UV-Vis spectra of Zn(II)Pc–polystyrene **4b** in chloroform (solid line) and chloroform/methanol mixtures (dashed lines). (C) Plot of the absorbance at 632 nm as a function of %methanol volume. (D) Plot of the absorbance at 682 nm as a function of % methanol volume



**Figure 5.** Transmission electron microscopy images of the aggregates formed by Zn(II)Pc–polystyrene **4a** (A) and **4b** (B, C, and D) in chloroform/methanol mixtures (v/v, 2/1)



Aggregate formation of **4a** and **4b** was further studied by transmission electron microscopy (TEM). Aggregate solutions were prepared by the slow addition of methanol to a chloroform solution (i.e.,  $10^{-4}$  M) of the Zn(II)Pc–polystyrene hybrids until a 2:1 (v/v) chloroform methanol ratio was achieved. Samples were prepared from a drop of the solution on carbon-coated grids and analyzed by TEM. Figure 5A shows an electron micrograph of the aggregates formed by Zn(II)Pc–polystyrene **4a** as large and solid spheres (i.e., 800–1000 nm in size). The same experiment with Zn(II)Pc–polystyrene **4b** resulted in the formation of small spherical aggregates (i.e., 20–80 nm in size, Fig. 5B, C, and D). The latter structures have a dark core that is surrounded by a lighter area, pointing to core–shell type morphologies, whereas the aggregates formed by **4a** are solid black spheres. The basis for the difference in aggregate morphology can be the average tail length for both materials: in Zn(II)Pc–polystyrene **4a**, this value is 15 times longer than the average tail length for **4b**. For Zn(II)Pc–polystyrene **4a**, the Pc head group does not seem to influence the aggregate formation, this material forming large, phase-separated polystyrene structures. However, for the compound with the shorter polystyrene tail **4b**, the  $\pi$ – $\pi$  stacking among the terminal Pc head group seems to drive the aggregation process into more organized architectures. These structures proved to be stable over time for more than 1 month.

## CONCLUSION

In the present study, it is shown that the polymerization of styrene by ATRP using a series of Zn(II)Pc initiators proceeds in a controlled fashion and yields well-defined Zn(II)Pc–polystyrene hybrids with low polydispersities. Compound **4b**, with the shortest polymer tail, forms well-organized spheres of 20–80 nm in size. Further studies are devoted to study encapsulation and catalytic properties of Pc–polystyrene architectures.

## EXPERIMENTAL SECTION

### General information

Chemicals were purchased from Aldrich Chemical Co. and used as received without further purification. Dry solvents were purchased from SDS in *anhydrous grade* and dried in addition, over molecular sieves (0.4 nm). Prior to use, the molecular sieves were dried in an oven for one night and subsequently activated by microwave oven-assisted irradiations alternating with vacuum treatment. NMR spectra were recorded with a BRUKER AC-300 apparatus (Bruker, The Netherlands). Deuterated solvent employed is indicated in brackets for each case. Chemical shift values ( $\delta$ ) are referred to tetramethylsilane, utilized as internal reference. UV–Vis spectra were recorded in solution by using solvents in *spectroscopic grade* on a Varian Cary 50 spectrophotometer, (Varian, Germany). Fourier transform infrared spectra were recorded on a Bruker Vector 22 spectrophotometer, (Bruker, The Netherlands). GPC measurements were performed with a Shimadzu GPC with Shimadzu refractive index and UV–Vis detectors, (Shimadzu, Japan) using tetrahydrofuran or  $\text{CHCl}_3$  as mobile phases. MALDI-TOF measurements were performed with a Kratos Kompact MALDI 4 instrument, (Kratos Analytical, Japan). GC was performed on a Varian 3800 GC instrument, (Varian, Germany) with a flame ionization detector using a Supelco fused silica column (15 m in length, 35  $\mu\text{m}$  in diameter, and  $d_f$  of 1.0  $\mu\text{m}$ ).

Samples for TEM from the aggregate solutions were prepared by dropping a drop of the solution on a carbon-coated grid placed on a filter paper, thereby directly drying of remaining solvent. TEM images were obtained with a JEOL JEM-1010 microscope (60 kV), (JEOL, Japan) equipped with a charge-coupled device camera.

### Synthesis of **2**, **3**, **9**, **10**, **16**, **17**-hexakis(*p*-*tert*-butylphenoxy)-**23**-(2-hydroxyethoxy)-phthalocyanine (**2**)

Finely divided lithium (0.004 g, 0.56 mmol) was added to a flask containing pentanol (6 ml). Once all the lithium was consumed, 4,5-bis(*p*-*tert*-butylphenoxy)phthalonitrile<sup>[37]</sup> (0.6 g, 1.4 mmol) and 4-(2-hydroxyethoxy)phthalonitrile<sup>[38]</sup> (0.09 g, 0.47 mmol) were added, and the mixture was heated to reflux under argon for 7 h. After cooling to room temperature, acetic acid (15 ml) was added, and the mixture was additionally stirred for 30 m. Water (30 ml) was then added, and the mixture of Pcs was extracted with  $\text{CH}_2\text{Cl}_2$ . After evaporation of the solvent, acetonitrile (15 ml) was added, and the solid material was filtered under vacuum. Column chromatography on silica gel using  $\text{CH}_2\text{Cl}_2$  : hexane (10:1)/ $\text{CH}_2\text{Cl}_2$  afforded metal-free phthalocyanine **1** as a green solid (115 mg, 17%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  8.6–8.0 (4  $\times$  m, 9H, *PcH*), 7.5–7.2 (m, 24H, *ArH*), 4.4 and 4.2 (2  $\times$  m, 4H,  $\text{OCH}_2\text{CH}_2\text{OH}$ ), 1.35 (m, 54H,  $\text{C}(\text{CH}_3)_3$ ) ppm. UV–Vis ( $\text{CHCl}_3$ )  $\lambda$ , 353, 615, 643, 671, 705 nm. MALDI-TOF-MS calcd for  $\text{C}_{94}\text{H}_{94}\text{N}_8\text{O}_8$  1462,72;  $m/z$  1462, 1463, 1464, 1465 (isotopic pattern M+).

### Synthesis of **2**, **3**, **9**, **10**, **16**, **17**-hexakis(*p*-*tert*-butylphenoxy)-**23**-(2-hydroxyethoxy)-phthalocyaninate zinc(II) (**1**)

Metal-free derivative **2** (115 mg, 0.078 mmol) was metallated by dissolving it in a mixture of  $\text{CHCl}_3$  and MeOH (3:1) (30 ml) together with an excess of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.07 g, 0.37 mmol), and the resulting reaction mixture was refluxed for 20 h. The crude was evaporated to dryness and redissolved in  $\text{CHCl}_3$ . The solution was washed extensively with water, and the organic layer was evaporated yielding **1** as a blue solid (115 mg, 97%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  8.8–7.6 (broad m, 9H, *PcH*), 7.5–6.9 (m, 24H, *ArH*), 4.5–3.2 (broad, 4H,  $\text{OCH}_2\text{CH}_2\text{OH}$ ), 1.4–1.2 (m, 54H,  $\text{C}(\text{CH}_3)_3$ ) ppm. UV–Vis ( $\text{CHCl}_3$ )  $\lambda$  346, 617, 685 nm. MALDI-TOF-MS calcd for  $\text{C}_{94}\text{H}_{92}\text{N}_8\text{O}_8\text{Zn}$  1524,63.  $m/z$  1524, 1525, 1526, 1527, 1528, 1529, 1530 (isotopic pattern M+).

### Synthesis of **2**, **3**, **9**, **10**, **16**, **17**-hexakis(*p*-*tert*-butylphenoxy)-**23**-(2-bromo-2-methylpropanoiloxy)-phthalocyaninate zinc(II) (**3**)

A solution of **1** (80 mg, 0.052 mmol) and triethylamine (100  $\mu\text{l}$ , 0.8 mmol) in dry dichloromethane was slowly added to 2-bromoisobutyl bromide (90  $\mu\text{l}$ , 0.72 mmol). The reaction mixture was stirred for 43 h. Subsequently, the organic layer was washed with water and evaporated to dryness. The crude reaction product was purified by silica column chromatography (silica, 4% MeOH/ $\text{CHCl}_3$ ), followed by a SEC (Biobeads, toluene), and finally, precipitation in methanol to yield **3** as a purple solid (76 mg, 87%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.5–7.5 (m, 9H, *PcH*), 7.4–7.0 (m, 24H, *ArH*), 4.60 and 4.28 (2  $\times$  s, 4H,  $\text{OCH}_2\text{CH}_2\text{OH}$ ), 1.94 (s, 6H,  $\text{C}(\text{CH}_3)_2\text{Br}$ ), 1.4–1.2 (m, 54H,  $\text{C}(\text{CH}_3)_3$ ) ppm. UV–Vis ( $\text{CHCl}_3$ )  $\lambda$  346, 617, 685 nm. MALDI-TOF MS calcd for  $\text{C}_{98}\text{H}_{97}\text{BrN}_8\text{O}_9\text{Zn}$  1672,59;  $m/z$  1672, 1673, 1674, 1675, 1676, 1677, 1678, 1679, 1680 (isotopic pattern M+).

### Atom transfer radical polymerization procedure for styrene polymerization (synthesis of **4a** and **4b**)

A Schlenk tube was charged with the Pc initiator **3** (20 mg, 0.012 mmol) and CuBr (1.7 mg, 0.012 mmol) and vacuum-nitrogen refilled three times. Subsequently, the Schlenk tube was capped with a septum, and styrene (4 ml) and anisole (2 ml) were added by a syringe. The resulting mixture was purged with nitrogen for 5 min and placed in an ice bath, after which pentamethyl diethylene triamine (5  $\mu\text{l}$ , 0.024 mmol) was added. Next, the tube was placed in an oil bath with a temperature of 90  $^\circ\text{C}$ , and the reaction mixture was sampled periodically to determine the ratio of styrene/anisole with GC. After polymerization, the mixture was dissolved in toluene and purified over a short size exclusion column (Biobeads S-X1) with toluene as eluent to remove traces of copper and unreacted monomer from the polymer batch.

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