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# Synthesis and self-assembly of oligomers containing cruciform 9,10-bis(arylethynyl)anthracene unit: formation of supramolecular nanostructures based on rod-length-dependent organization



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## ABSTRACT

Conjugated rod-coil molecules, incorporating flexible and rigid blocks, have a strong affinity to selforganize into various supramolecular nanostructures in the bulk state. In this study, we report synthesized oligomers containing cruciform 9,10-bis(arylethynyl)anthracene units and characterized their selfassembly behavior. The molecular structures were characterized with <sup>1</sup>H, <sup>13</sup>C NMR, and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy. An investigation of the supramolecular nanostructures of these molecules using differential scanning calorimetry, thermal polarized optical microscopy, and small-angle X-ray scattering revealed that the rod length of coil-rod-coil molecules with identical rod to coil volume ratios dramatically influences self-assembly behavior in the bulk state. Molecules **2** and **3** with relatively longer rod lengths self-assemble into lamellar structures in the solid state, whereas, molecules **1** and **4** self-assemble into two-dimensional (2-D) oblique columnar structures in the liquid crystalline phase, in addition, on heating, molecule **1** transforms from the oblique columnar phase to the nematic phase.

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# 1. Introduction

Synthesis of supramolecular units through self-assembly is one of the most exciting interdisciplinary researches areas involving chemistry, biology, and material science.<sup>1</sup> Among self-assembling molecular systems, rod-coil block molecules consisting of an elongated rigid rod and a flexible coil have attracted attention as interesting self-assembling soft materials given the possibility of synthesizing novel functional materials by combining their selfassembling capability and functional uniqueness.<sup>2</sup> Self-assembly studies concerning supramolecular structures and their intriguing properties have been reported, with a focus on the various shapes of the rigid conjugated rod segment, such as Y-,<sup>3</sup> T-,<sup>4</sup> O-,<sup>5</sup> K-,<sup>6</sup> propeller-,<sup>7</sup> and dumbbell-shaped<sup>8</sup> rod-coil molecules. Precise control over a supramolecular nanostructure with a well-defined shape and size is of critical importance for their application in photoelectronic self-organizing materials. This control is achieved by adjusting the cooperative effects of various molecular parameters such as volume fraction of rod to coil segment, rod anisotropy, and coil cross-sectional area.<sup>9</sup> Anthracene-centered cruciform compounds have been studied widely, with a focus on their two-photon absorption (TPA) properties;<sup>2b,10</sup> however, there are few studies on the self-assembling behavior of anthracene-centered cruciform derivates that explore the relationship between molecular aggregates and their unique physical properties. Therefore, it is interesting to design and synthesize new types of cruciform compounds possessing excellent TPA properties and study their self-assembling behavior for improving molecular photoelectronic properties.

With this in mind, we synthesized coil-rod-coil molecules **1–4** (Scheme 1) with conjugated rod building blocks and investigated their self-assembly behaviors in the bulk state with differential scanning calorimetry (DSC), thermal polarized optical microscopy (POM), and small-angle X-ray scattering (SAXS).

# 2. Results and discussion

# 2.1. Synthesis and characterization of molecules 1-4

The synthetic route of cruciform 9,10-bis(arylethynyl)anthracene derivatives consisting of 9,10-bis(arylethynyl)anthracene as

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Scheme 1. Chemical structures of the molecules 1–4 based on anthracene aromatic rod building block.

a rigid rod segment connecting poly(ethylene oxide) (PEO) chains of different lengths is outlined in Scheme 2. Target molecules were obtained through successive reaction steps including tosylation, substitution reaction, methylation, demethylation reaction, and Sonogashira coupling reaction. Target molecules **1–4** were characterized with <sup>1</sup>H, <sup>13</sup>C NMR and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy and were shown to be in full agreement with the structures presented in Scheme 1. A representative <sup>1</sup>H NMR spectrum analysis of molecule **1** is shown in Fig. 1 (three other

molecular <sup>1</sup>H, <sup>13</sup>C NMR spectra are shown in Figs. S1–7, and <sup>1</sup>H–<sup>1</sup>H COSY and NOESY spectra of molecule **1** are shown in Figs. S8 and 9, see Supplementary data). As confirmed by <sup>1</sup>H NMR spectroscopy, the ratio of the aromatic protons of the rod block to the alkoxyl protons is consistent with the calculated value, and the MALDI-TOF mass spectra of the molecules show three signals that can be assigned to H<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> labeled molecular ions (Fig. S10, see Supplementary data). The experimental mass based on peak positions in the spectrum is well matched with the theoretical molecular weight of each molecule.



Scheme 2. Synthetic route of molecules 1-4.



Fig. 1. <sup>1</sup>H NMR spectrum of molecule 1 (solvent: CDCl<sub>3</sub>).

### 2.2. Structural analysis in bulk state

The self-assembly behavior of **1–4** was investigated with DSC, POM, and XRD in the bulk state. Fig. 2 shows the DSC heating and cooling traces of molecules **1–4**. The transition temperatures of molecules **1–4** obtained from the DSC heating and cooling scans are summarized in Table 1.



**Fig. 2.** DSC traces (10 °C/min) recorded during the second heating and the first cooling scans of molecules **1–4**.

#### Table 1

Thermodynamic transformation of molecules **1–4** (data are from the second heating and the first cooling scans)

Molecule	$f_{\rm coil}$	Phase transition temperature (°C)		
		Heating	Cooling	
1	0.48	k 56.1 Col <sub>o</sub> 95.9 N 132.2 i	i 123.7 N 76.1 Col <sub>o</sub>	
2	0.48	L 240.5 i	i 272.7 L	
3	0.48	L 269.4 i	i 262.3 L	
4	0.38	k 95.9 Col <sub>o</sub> 146.6 i	i 126.3 Col <sub>o</sub>	

k: crystalline phase; L: lamellar; Col<sub>o</sub>: oblique columnar; N: nematic phase; i: isotropic phase,  $f_{coil}$ : coil volume fraction.

On heating, molecule **1** melts into a liquid crystalline phase at 56.1 °C and then into a second liquid crystalline phase, which in turn undergoes isotropization at 132.2 °C (Fig. 2A). On the slow cooling of molecule **1** from the isotropic liquid to liquid crystalline mesophase, a schlieren-like texture is observed in the POM experiment. This corresponds to a nematic liquid crystalline phase (Fig. 3A). A schematic diagram of the nematic phase of molecule **1** is shown in Fig. 5A. As the temperature decreases further, a focal. conical, fan-shaped spherulitic texture is observed, which preliminarily confirms the presence of a 2-D ordered columnar phase (Fig. 3B). As the sample is cooled to room temperature, the liquid crystalline phase transforms into a crystalline phase (Fig. 3C). To corroborate the detailed liquid crystalline structure of molecule 1, we performed SAXS experiments at various temperatures during cooling from the isotropic phase to the solid state. Fig. 4A shows the X-ray diffraction patterns of molecule 1 at 80 °C; the SAXS profile of molecule 1 shows a number of Bragg reflections, which can be assigned to a 2-D oblique columnar structure with lattice parameters a=4.7 nm, b=2.9 nm, and  $\gamma=63^{\circ}$  (Table 2). For obtaining detailed information on the packing arrangement, we calculated the number (n) of molecules in a single slice of the column. From the experimental values of the unit cell parameters  $(a, b, c, and \gamma)$  and density  $(\rho)$ , the average number of molecules per cross-sectional slice of the column can be calculated using Eq. 1, where *M* is the molecular mass and NA is Avogadro's number. The number of molecules in a single slice of the column, calculated based on the lattice constants and measured densities of molecule 1, is about 4 (implying an equal number of molecules per columnar cross section irrespective of the PEO chain length). On the basis of this data. a schematic representation of the oblique columnar structure of molecule 1 is shown in Fig. 5B.

$$n = \frac{abc\rho\sin\gamma N_{\rm A}}{M} \tag{1}$$

To further evaluate the influence of rod length on the selfassembly behaviors of coil-rod-coil molecules, we synthesized coil-rod-coil molecules 2 and 3, and investigated their selfassembly behaviors in the bulk state. In sharp contrast to molecule 1, molecules 2 and 3 show the solid phase and transform into an isotropic liquid at 240.5 °C and 269.4 °C, respectively (Fig. 2B and C). Upon slow cooling from the isotropic liquid temperature to room temperature, these two molecules exhibit a wide range of crystallization phenomena in the field of vision. Notably, the melting point of molecules 1-3 with different rod lengths but identical rod to coil volume ratios, as shown in Fig. 2, increases as the length of the conjugated rod segment increases. This can be ascribed to the fact that the extended conjugated rod segment enhances intermolecular  $\pi - \pi$  interaction, thereby increasing the melting points of those coil-rod-coil molecules. The small-angle XRD patterns of molecules 2 and 3 contain several sharp reflections. These reflections correspond to equidistant q-spacing (Fig. 4B and C) and can be indexed to a lamellar lattice with the layer spacing of 4.6 nm and 5.1 nm, respectively. Considering the estimated molecular lengths (9.8 nm and 11.4 nm using the CPK model for molecules 2 and 3, respectively), the PEO coil segments of molecules 2 and 3 are fully interdigitated and the rod segments are packed in a monolayer arrangement (Fig. 5C).

To investigate the effect of molecules with the same building block rod length but different PEO coil chain lengths on the selfassembly behavior of this molecular architecture, we synthesized coil segments of the coil-rod-coil molecule **4** consisting of poly(ethylene oxide) with a degree of polymerization of 3. Similar to molecule **1**, molecule **4** also displays a columnar mesophase in the liquid crystalline phase. The DSC results show that the crystal melting transition involves a birefringent liquid crystalline phase at



Fig. 3. Representative optical polarized micrographs of the texture exhibited by (A) nematic phase of 1 at the transition from the isotropic liquid, (B) oblique columnar structure of 1 in the liquid crystalline phase, (C) the crystalline phase of 1, (D) oblique columnar structure of 4 in the liquid crystalline phase.



**Fig. 4.** Small-angle X-ray diffraction patterns of (A) oblique columnar structure on cooling to 80 °C for molecule **1**, (B) lamellar structure at 100 °C for molecule **2**, (C) lamellar structure at 90 °C for molecule **3**, (D) oblique columnar structure on cooling to 110 °C for molecule **4**.

95.9 °C, followed by an isotropic phase at 146.6 °C (Fig. 2D). In addition, upon cooling from the isotropic liquid temperature, a fanshaped spherulitic texture can be observed. This indicates the presence of a two-dimensional (2D) ordered columnar phase (Fig. 3D). As shown in Fig. 4D, in the liquid crystalline phase, the corresponding small-angle XRD patterns show several reflections, which can be indexed as the (100), (110), (010), (210), and (200)

# Table 2

Small-angle X-ray diffraction data for oblique columnar structure for molecule 1 (measured at 80  $^\circ$ C)

h	k	1	$q_{\rm obsd}~({\rm nm}^{-1})$	$q_{ m calcd} ({ m nm}^{-1})$
1	0	0	1.520	1.523
1	1	0	2.220	2.219
0	1	0	2.461	2.461
2	1	0	2.923	2.937
2	0	0	3.050	3.042

 $q_{\rm obsd}$  and  $q_{\rm calcd}$  are the scattering vectors of the observed and calculated reflections for the oblique columnar structure with lattice parameters a=4.7 nm, b=2.9 nm,  $\gamma$ =63° ( $\lambda$ =0.154 nm).

planes of a 2D oblique columnar structure with lattice parameters a=4.5 nm, b=2.8 nm, and  $\gamma$ =63° (Table 3). The number of molecules in a single slice of the column, calculated according to Eq. 1, is about 4. Compared with molecule **1**, the nematic liquid crystalline phase is not observed for molecule **4**, which is due to the reduction in rod to coil volume fraction from 0.48 to 0.38.

On the basis of the above discussion, we draw the interesting conclusion that molecules 1-3 have different rod lengths but equal rod to coil volume ratios. Molecule 1 self-assembles into oblique columnar and nematic aggregates in the liquid crystalline phase. However, molecules 2 and 3 with longer rod segments selfassemble into lamellar structures in the solid state (Table 4), although these molecules have equal rod to coil segment volume fractions. As mentioned in the Introduction, generally, the volume fraction of rod to coil segment, rod anisotropy, and coil crosssectional area influence the self-assembly behaviors of supramolecular nanostructures. For the rod-coil molecule system, rod to coil volume ratio is a major parameter for constructing various supramolecular nanostructures. Hence, we can attribute the selfassembly behavior of molecules 1-3, which have different rod lengths but identical rod to coil volume ratios, to microphase separation between the rod and coil domains of the molecules due to different driving forces of the  $\pi - \pi$  stacking interaction. Compared with molecule 1, which has a relatively short conjugated rod length, the driving force of the  $\pi$ - $\pi$  stacking interactions of molecules **2** and **3** is slightly stronger. Subsequently, this affects the construction of supramolecular nanostructures. The DSC results of molecules



Fig. 5. Schematic representation of self-assembly of (A) nematic phase and (B) oblique columnar structure of molecule 1, and (C) lamellar structure of molecule 2.

Table 3 Small-angle X-ray diffraction data for oblique columnar structure for molecule 4 (measured at 110  $^{\circ}$ C)

h	k	1	$q_{\rm obsd}  ({\rm nm}^{-1})$	$q_{ m calcd}  ({ m nm^{-1}})$
1	0	0	1.556	1.552
1	1	0	2.259	2.260
0	1	0	2.491	2.491
2	1	0	2.969	2.971
2	0	0	3.104	3.118

 $q_{\rm obsd}$  and  $q_{\rm calcd}$  are the scattering vectors of the observed and calculated reflections for the oblique columnar structure with lattice parameters a=4.5 nm, b=2.8 nm,  $\gamma$ =63° ( $\lambda$ =0.154 nm).

# Table 4

Summary of small-angle X-ray diffraction data for molecules 1-4

Molecule	Crystalline phase	Liquid crystalline phase			
	Lamellar (L) d (nm)	Oblique columnar structure (Col <sub>o</sub> )			
		<i>a</i> (nm)	<i>b</i> (nm)	γ	n
1		4.7	2.9	63	4
2	4.6				
3	5.1				
4		4.5	2.8	63	4

*d*, the layer spacing; *a*, *b*, lattice constant (nm);  $\gamma$ , characteristic angle; *n*, the average number of molecules per cross-sectional slice of the column.

1–3 indirectly demonstrate the point that the extended conjugated rod segment enhances intermolecular  $\pi - \pi$  interaction, thereby leading to an increase in the melting points of those coil-rod-coil molecules. It should be pointed out that we have reported the synthesis and self-assembly behavior of coil-rod-coil molecules with lateral methyl and ethyl groups in the center of the rod segment. The experimental results reveal that the lateral alkyl group in the middle of the rod segment dramatically influences selfassembly behavior in the liquid crystalline phase. Compared with rod-coil molecules without side chains, rod-coil molecules with lateral alkyl groups in the middle of rod segments lead to 2D or 3D self-assembly. Generally, linear rod-coil molecules without lateral rod groups and a rod to coil volume fraction of approximately 0.5 self-assemble into lamellar structures or isotropic liquid in the solid state and melt state, respectively,<sup>11</sup> whereas molecules 1 and 4 selforganize into 2D columnar nanostructures in the liquid crystalline phase. This behavior is reasonable considering the influence of the two benzene groups of cruciform 9,10-bis(arylethynyl)anthracene outside the linear rod segment. Compared with rod-coil molecules without a lateral alkyl group in the center of the rod segment and equal rod to coil volume fractions, the driving force of the intermolecular  $\pi - \pi$  interaction of molecules **1** and **4** decreases due to the two benzene groups that are outside the linear rod building block. This leads to the formation of the 2D columnar mesophase in the melt state. Therefore, the coil to rod volume fraction, presence of lateral alkyl or benzene groups in the middle of rod segment, and rod segment length collaboratively contribute to the construction of supramolecular nanostructures with a well-defined size and shape for rod-coil molecular systems.

# 3. Conclusions

Cruciform molecules **1–4** consisting of 9,10-bis(arylethynyl) anthracene as a rigid rod segment connecting PEO chains of various lengths were synthesized, characterized, and their self-assembly behavior was investigated in the bulk state. The experimental results reveal that the rod length of coil-rod-coil molecules with equal rod to coil volume ratios dramatically influences their self-assembly behavior in the bulk state. Furthermore, the benzene units of cruciform 9,10-bis(arylethynyl)anthracene in the center of rod building block have the same effect. Molecules **2** and **3** with relatively longer PEO coil chains self-assemble into a lamellar structure in the solid state, whereas molecules **1** and **4** with relatively short PEO chains self-assemble into 2D oblique columnar structures in the liquid crystalline phase. In addition, on heating, molecule **1** transforms from an oblique columnar structure to the nematic phase.

# 4. Experimental

# 4.1. Materials

All reagents were obtained from Sigma—Aldrich, Acros, and TCI Chemical Co. and used as received. Trimethylsilyl-acetylene, tetrakis(triphenyl-phosphine) palladium(0), iodomethane, 4hydroxy-4'-iodobiphenyl, cuprous iodide, 2-methyl-3-butyn-2-ol, 4-iodophenol, toluene-*p*-sulfonyl chloride (TsCl, 98%), 9,10dibromoanthracene, 2-methoxyethanol, tetraethylene glycol, triethylene glycol-monomethyl ether, 4,4'-diiodobiphenyl, and conventional reagents were used as received. Tetrahydrofuran (THF) was distilled from sodium metal at the presence of benzophenone and degassed prior to use. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry N<sub>2</sub>.

# 4.2. Techniques

Flash column chromatography was performed using silica gel (200–300 mesh). <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra were recorded in CDCl<sub>3</sub> on Bruker AM-300 instruments. Chemical shifts were described in parts per million (ppm) ( $\delta$  units) downfield of tetramethylsilane (TMS) as an internal standard and the coupling constants (*J* values) were reported in hertz (Hz). Reference values for residual solvent were taken as  $\delta$ =7.27 (CDCl<sub>3</sub>) for <sup>1</sup>H NMR;  $\delta$ =77.1 (CDCl<sub>3</sub>) for <sup>13</sup>C NMR. Multiplicities for coupled

signals are designated using the following abbreviations: s=singlet, d=doublet, t=triplet, m=multiplet. Two-dimensional <sup>1</sup>H-<sup>1</sup>H COSY and <sup>1</sup>H-<sup>1</sup>H NOESY techniques were measured using standard micro-programs provided by Bruker. A Perkin-Elmer Pyris Diamond differential scanning calorimeter was used to determine the thermal transitions, which were reported as the maxima and minima of their endothermic or exothermic peaks: the heating and cooling rates were controlled to 10 °C/min under N<sub>2</sub> atmosphere. The SAXS measurements were performed in transmission mode with synchrotron radiation at the 1W2A X-ray beam line at Beijing Accelerator Laboratory. A Nikon Optiphot 2-pol optical polarized microscope, equipped with a Mettler FP 82 hot-stage and a Mettler FP90 central processor, was used to observe the thermal transitions and to analyze the anisotropic texture. MALDI-TOF-MS was performed on a percaptive Biosystems Voyager-DESTR using a 2cyano-3-(4-hydroxyphenyl) acrylic acid (CHCA) as matrix.

# 4.3. Synthesis of molecules 1-4

Molecules **1–4** were synthesized using the same procedure. A representative example is described for molecule **1**.

Compound **6** (150 mg, 0.66 mmol) and compound **9** (725 mg, 1.98 mmol) were added to tetrahydrofuran (40 mL). Triethylamine (20 mL) was added and then tetrakis(triphenyl-phosphine)palladium(0) (23 mg, 19.8 mmol) and copper iodide (5 mg, 26.4 mmol) were added. The mixture was degassed and then heated at reflux for 48 h with vigorous stirring under nitrogen. The solvent was removed in a rotary evaporator and the resulting mixture was poured into water and extracted with dichloromethane, dried over anhydrous magnesium sulfate, and filtered. The solvent was evaporated to dryness. The crude product was purified by column chromatography (silica gel) using methylene dichloride/ethyl acetate (1:3 v/v) as eluant to yield a red solid (0.19 g, 35%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.72 (dd, *J*=6.6 and 3.2 Hz, 4H, Ar), 7.82 (d, *J*=8.4 Hz, 4H, Ar), 7.57–7.67 (m, 12H, Ar), 7.03 (d, *J*=8.8 Hz, 4H, Ar), 4.18 (*t*, *J*=4.6 Hz, 4H, 2phenylOCH<sub>2</sub>CH<sub>2</sub>O), 3.91 (t, *J*=4.6 Hz, 4H, 2phenylOCH<sub>2</sub>CH<sub>2</sub>O), 3.91 (t, *J*=4.6 Hz, 4H, 2phenylOCH<sub>2</sub>CH<sub>2</sub>O), 3.54–3.75 (m, 32H, 2phenyl-OCH<sub>2</sub>CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>4</sub>CH<sub>3</sub>), 3.38 (s, 6H, 2OCH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 158.5, 140.7, 133.1, 131.9, 128.1, 127.1, 126.7, 121.6, 118.3, 115.1, 102.4, 71.9, 70.7, 69.7, 67.6, 58.9. MALDI-TOF-MS *m*/*z* [M]<sup>+</sup> 1031.

*Molecule* **2**: red solid, 32%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.75 (dd, *J*=6.6 and 3.2 Hz, 4H, Ar), 7.88 (d, *J*=8.2 Hz, 4H, Ar), 7.60–7.75 (m, 16H, Ar), 7.51 (d, *J*=8.5 Hz, 4H, Ar), 6.93 (d, *J*=8.5 Hz, 4H, Ar), 4.18 (t, *J*=4.3 Hz, 4H, 2phenylOCH<sub>2</sub>CH<sub>2</sub>O), 3.89 (t, *J*=4.3 Hz, 4H, 2phenylOCH<sub>2</sub>CH<sub>2</sub>O), 3.52–3.82 (m, 46H, 2phenyl-OCH<sub>2</sub>CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>6</sub>CH<sub>3</sub>), 3.39 (s, 6H, 2OCH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 159.0, 140.6, 139.7, 133.1, 132.2, 132.0, 127.2, 127.0, 126.9, 123.2, 118.6, 115.5, 114.7, 102.3, 90.4, 88.0, 87.6, 71.9, 70.9, 70.6, 69.6, 58.9. MALDI-TOF-MS *m*/*z* [M]<sup>+</sup> 1406, [M+Na]<sup>+</sup> 1429, [M+K]<sup>+</sup>1445.

*Molecule* **3**: red solid, 40%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.71 (dd, *J*=6.6 and 3.2 Hz, 4H, Ar), 7.84 (d, *J*=8.0 Hz, 4H, Ar), 7.52–7.71 (m, 28H, Ar), 6.99 (d, *J*=8.6 Hz, 4H, Ar), 4.17 (t, *J*=4.4 Hz, 4H, 2phenylOCH<sub>2</sub>CH<sub>2</sub>O), 3.88 (t, *J*=4.4 Hz, 4H, 2phenylOCH<sub>2</sub>CH<sub>2</sub>O), 3.50–3.81 (m, 56H, 2phenylOCH<sub>2</sub>CH<sub>2</sub>O(*CH*<sub>2</sub>CH<sub>2</sub>O)<sub>7</sub>CH<sub>3</sub>), 3.38 (s, 6H, 2OCH<sub>3</sub>). <sup>13</sup>C NMR (65 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 159.3, 140.7, 132.9, 132.2, 132.1, 131.9, 127.9, 127.0, 126.9, 126.5, 120.0, 115.0, 102.4, 90.9, 88.1, 87.7, 71.9, 70.9, 70.6, 69.7, 67.6, 59.1. MALDI-TOF-MS *m*/*z* [M]<sup>+</sup> 1648, [M+Na]<sup>+</sup> 1671.

*Molecule* **4**: red solid, 42%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.73 (dd, *J*=6.6 and 3.2 Hz, 4H, Ar), 7.86 (d, *J*=8.4 Hz, 4H, Ar),

7.58–7.70 (m, 12H, Ar), 7.04 (d, *J*=8.8 Hz, 4H, Ar), 4.20 (t, *J*=4.6 Hz, 4H, 2phenylOCH<sub>2</sub>CH<sub>2</sub>O), 3.92 (t, *J*=4.6 Hz, 4H, 2phenylOCH<sub>2</sub>CH<sub>2</sub>O), 3.51–3.81 (m, 15H, 2phenylOCH<sub>2</sub>CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>CH<sub>3</sub>), 3.34 (s, 6H, 2OCH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 158.7, 132.0, 130.3, 128.6, 128.2, 127.4, 126.5, 121.5, 119.5, 115.2, 102.4, 72.1, 71.2, 70.7, 70.2, 67.3, 58.9. MALDI-TOF-MS *m*/*z* [M]<sup>+</sup> 854.

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# Supplementary data

Procedure of the synthetic reaction, and spectroscopic data diagrams of all products **5–14**. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/ 10.1016/j.tet.2013.12.072.

# **References and notes**

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