

Electronic Supplementary Material (ESI)

# **Synthesis of poly(3-hexylthiophene) based rod-coil conjugated block copolymers via photoinduced metal-free atom transfer radical polymerization**

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## Experimental

### Materials

3-Hexylthiophene (99+%), *N*-bromosuccinimide (99%), iodine (99.8+%), iodobenzene diacetate (98%), methyl methacrylate (MA, 99%) and 2-(dimethylamino)ethyl methacrylate (DMAEMA, 99%) were purchased from Acros Organics (Bridgewater, NJ, USA). Ni(dppp)Cl<sub>2</sub> (97+%), *i*-PrMgCl in THF (2 mol/l) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and stored in glove box at room temperature. 2-Bromoisobutyl bromide (Br-*i*BuBr, 98%), triethylamine (NEt<sub>3</sub>, 99%), *N,N*-diisopropylethylamine (99%), anhydrous *N,N*-dimethylformamide (DMF, 99.8%), sodium borohydride (NaBH<sub>4</sub>, 99%), phosphorus(V)oxychloride (POCl<sub>3</sub>, 99%), pyrene (98%), methacryloyl chloride (97%) and pyrene-1-ylmethanol (PM, 98%), phenothiazine (98+%), sodium *tert*-butoxide (NaOtBu, 97%), palladium(II) acetate (Pd(OAc)<sub>2</sub>), tri-*tert*-butylphosphine (98%), 1-bromopyrene (96%), cyanuric chloride (99%), 2-hydroxyethyl methacrylate (98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Chloroform (CHCl<sub>3</sub>, 99%), toluene (99%), tetrahydrofuran (THF, 99%) were purchased from Labscan Ltd. (Asia, Thailand) and distilled under N<sub>2</sub> before use. Dichloromethane (Chem-Laboratory, 99.8%), *n*-heptane (Labscan, 99%), *n*-hexane (Labscan, 99%), and methanol (99.8%) were used as received.

### Characterization and instrumentation

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in deuterated chloroform (CDCl<sub>3</sub>) with TMS as an internal reference, on a Bruker Avance 500 MHz spectrometer. FT-IR spectra, collected as the average of 64 scans with a resolution of 4 cm<sup>-1</sup>, were recorded from KBr disk on a FT-IR Bruker Tensor 27. MALDI TOF analysis was performed using a Voyager Elite apparatus in linear mode using trans-2-[3-(4-*tert*butylphenyl)-2-methylprop-2-enylidene]-malo- nitrile (DCTB) as matrix. Nitrogen laser desorption at a wavelength equal to 337 nm was applied. Size exclusion chromatography (SEC) measurements were performed on a Polymer PL-GPC 50 gel permeation chromatograph system equipped with an RI detector, with THF as the eluent at a flow rate of 1.0 mL/min. Molecular weights and molecular weight distributions were calculated with reference to polystyrene standards. For UV light induced metal-free ATRP reactions, the reaction flask was irradiated at room temperature by a 365 nm UV light (12 x 9 watt bulbs, intensity of 2.2 mW cm<sup>-2</sup> determined by a VLX365 radiometer) lamp set-up. Another UV lamp with intensity of 0.05 mW/cm<sup>2</sup> determined by a VLX365 radiometer was also tested for DMAEMA polymerization. For visible-light induced metal-Free ATRP of DMAEMA, the reaction flask was irradiated

at room temperature by a 465 nm VIS light (10 x 4 lumen bulbs circularly oriented, intensity of 0.06 mW/cm<sup>2</sup> determined by a Extech LT45 light meter) lamp set-up.

### Synthesis of 2-bromo-3-hexylthiophene

To a solution of 3-hexylthiophene (5 g, 29.7 mmol) in anhydrous THF (50 mL) in a 200 mL flask, a solution of *N*-bromosuccinimide (5.29 g, 29.7 mmol) was added slowly at 0 °C under nitrogen. The mixture was stirred at 0 °C for 1 h. After that, 50 mL of distilled water was added to the reaction mixture, and the mixture was extracted with diethyl ether. The organic layer was washed with a solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10%), a solution of KOH (10%), and dried over anhydrous MgSO<sub>4</sub>. The organic layer was distilled to give a colorless oil (6.7 g, 92%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm): 7.19 (d, *J* = 5.6 Hz, 1H), 6.82 (d, *J* = 5.6 Hz, 1H), 2.59 (t, *J* = 7.3 Hz, 2H), 1.59 (m, br, 2H), 1.33 (m, none, 6H), 0.91 (t, *J* = 6.2 Hz, 3H). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>), d (ppm): 141.0, 128.2, 125.1, 108.8, 31.6, 29.7, 29.4, 28.0, 22.6, 14.1.

### Synthesis of 2-bromo-3-hexyl-5-iodothiophene

Iodine (1.42 g, 11.18 mmol) and iodobenzene diacetate (1.965 g, 6.1 mmol) were added to a solution of 2-bromo-3-hexylthiophene (2.5 g, 11.1 mmol) in dichloromethane (25 mL) at 0 °C. The mixture was stirred at room temperature for 4 h. Then, aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10%) was added, and the mixture was extracted with diethyl ether and dried over anhydrous MgSO<sub>4</sub>. The solvent was evaporated to obtain crude product, which was purified by silica column chromatography (eluent: *n*-heptane) to give pure 2-bromo-3-hexyl-5-iodothiophene as a pale yellow oil (3 g, 86%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm): 6.97 (s, 1H), 2.52 (t, *J* = 7.54 Hz, 2H), 1.56 (quint, 2H), 1.32 (m, 6H), 0.89 (t, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>), d (ppm): 144.3, 137.0, 111.7, 71.0, 31.5, 29.6, 29.2, 28.8, 22.5, 14.1.

### Synthesis of regioregular head-to-tail poly(3-hexylthiophene) with H/Br end groups (polymer 4)

A dry, 500 mL three-neck flask was flushed with nitrogen and was charged with 2-bromo-3-hexyl-5-iodothiophene (24.37 g, 65 mmol). After three azeotropic distillations by toluene, anhydrous THF (220 mL) was added via a syringe, and the mixture was stirred at 0 °C for 1 h. *i*-PrMgCl (2 M solution in THF, 30.87 mL, 61.75 mmol) was added via a syringe and the mixture was continuously stirred at 0 °C for 1 h. The reaction mixture was allowed to cool down to 0 °C. The mixture was transferred to a flask containing a suspension of Ni(dppp)Cl<sub>2</sub> (650 mg, 1.20 mmol) in THF (25 mL). The polymerization was carried out for 24 h at 0 °C, followed by addition of 5 M HCl. After termination, the reaction was stirred

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for 15 min and extracted with  $\text{CHCl}_3$ . The polymer was precipitated in cold methanol and washed several times with *n*-hexane. The polymer was characterized by  $^1\text{H}$  NMR and GPC. Yield: 72%.

FT-IR ( $\text{cm}^{-1}$ ): 721, 819, 1376, 1454, 1510, 2853, 2922, 2953, 3056.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 6.96 (s, 1H), 2.90 (t,  $J = 7.5$  Hz, 2H), 1.79 (m, 2H), 1.52-1.30 (m, 6H), 0.94 (t,  $J = 6.4$  Hz, 3H). Maldi-ToF ( $m/z$ ): 1410, 1576, 1742, 1908, 2074, 2240, 2406, 2572, 2738, 2904, 3070, 3236. GPC:  $M_n = 8100$  g  $\text{mol}^{-1}$ ; polydispersity index ( $\text{Đ}$ ) = 1.11. UV-vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}} = 450$  nm.

### **Synthesis of regioregular head-to-tail poly(3-hexylthiophene) with CHO/Br end groups (polymer 5)**

Polymer 4 (1 g) was dissolved in 260 mL of anhydrous toluene under nitrogen. DMF (5.12 mL, 66.3 mmol) and phosphorus(V) oxychloride ( $\text{POCl}_3$ ) (5.30 mL, 58 mmol) were then added to the solution. The reaction was performed at 75 °C for 24 h. The solution was cooled down to room temperature, followed by the addition of a saturated aqueous solution of sodium acetate. The solution was stirred for 4 h. Then, the polymer was extracted with  $\text{CHCl}_3$ . The polymer was precipitated in cold methanol and washed with cold *n*-hexane. After drying under vacuum. The yield: 93%.

FT-IR ( $\text{cm}^{-1}$ ): 721, 819, 1376, 1453, 1509, 1649, 2854, 2923, 2953, 3056.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 9.99 (s, 1H), 6.96 (s, 1H), 2.78 (t, 2H), 1.69 (quint, 2H), 1.49-1.28 (m, 6H), 0.89 (t, 3H). Maldi-ToF ( $m/z$ ): 1602, 1768, 1934, 2100, 2266, 2432, 2598, 2764, 2930, 3096, 3262.

### **Synthesis of regioregular head-to-tail poly(3-hexylthiophene) with $\text{CH}_2\text{OH}$ /Br end group (polymer 6)**

Polymer 5 (500 mg) was dissolved in 30 mL of anhydrous THF under nitrogen.  $\text{NaBH}_4$  (41.8 mg) was then added. The mixture was kept stirring at room temperature for 2 h. Then, the solvent was evaporated under vacuum. The polymer was precipitated in cold methanol. After drying under vacuum, 480 mg of the polymer was obtained. Yield: 96%.

FT-IR ( $\text{cm}^{-1}$ ): 724, 817, 1376, 1453, 1509, 1561, 2853, 2922, 2953, 3056.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 6.96 (s, 1H), 4.8 (s, 2H), 2.78 (t, 2H), 1.69 (quint, 2H), 1.49-1.28 (m, 6H), 0.89 (t, 3H). Maldi-ToF ( $m/z$ ): 1440, 1606, 1772, 1938, 2104, 2270, 2436, 2602, 2768, 2934, 3100.

### **Synthesis of bromoester-terminated poly(3-hexylthiophene) (P3HT-macroinitiator) (polymer 7)**

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Polymer 6 (500 mg) was dissolved in 20 mL of anhydrous THF under nitrogen. To this solution, triethylamine (1 mmol) and 2-bromoisobutryl bromide (0.83 mmol) were added. Then, the reaction was carried out at 50 °C overnight. The polymer was extracted by CHCl<sub>3</sub>. The solution was washed two times with distilled water. The polymer was precipitated in cold methanol. After drying under vacuum, 475 mg of the polymer was obtained. The yield was 95%.

FT-IR (cm<sup>-1</sup>): 724, 818, 1376, 1451, 1509, 1561, 1735, 2853, 2922, 2953, 3056. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 6.96 (s, 1H), 5.29 (s, 2H), 2.78 (t, 2H), 1.93 (s, 6H), 1.69 (quint, 2H), 1.49-1.39 (m, 2H), 1.39-1.28 (m, 4H), 0.89 (t, 3H). Maldi-ToF (m/z): 1420, 1586, 1752, 1918, 2084, 2250, 2416, 2582, 2748, 2914, 3080. GPC:  $M_n$  = 8100 g mol<sup>-1</sup>,  $\bar{D}$  = 1.18.  $M_n$  estimated by <sup>1</sup>H NMR = 9000 g mol<sup>-1</sup>.

### Synthesis of 10-(pyren-1-yl)-10H-phenothiazine (PPTH)

A 25 mL storage flask was charged with a magnetic stir bar, flamed under vacuum and back-filled with nitrogen three times. The flask was then charged with phenothiazine (160 mg, 0.81 mmol, 1.00eq), NaOtBu (116 mg, 1.20 mmol, 1.5 eq.), Pd(OAc)<sub>2</sub> catalyst (3.61 mg, 0.016 mmol, 2 mol %), tri-*tert*-butylphosphine (6.50 mg, 0.032 mmol, 4 mol %) and dry toluene (8 mL). The flask was evacuated and back-filled three times with nitrogen before 1-bromopyrene (271 mg, 0.96 mmol, 1.2 eq.) was added. The flask was then placed in an oil bath at 110 °C while stirring for 4 h. The flask was then cooled to room temperature, diluted with CHCl<sub>3</sub>, washed with water, brine, dried with K<sub>2</sub>SO<sub>4</sub>, and purified using column chromatography (5 % EtOAc/hexane). The product was dried under reduced pressure to yield 230 mg of a yellow solid (72 % yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.39 (d, 1H, Py-H), 8.32 (d, 1H, Py-H), 8.27 (d, 1H, Py-H), 8.24 – 8.04 (m, 6H, Py-H), 7.08 (dd, 2H), 6.79 (td, 2H), 6.66 (td, 2H), 5.97 (dd, 2H).

### Synthesis of 2-([4,6-dichlorotriazin-2-yl]oxy)ethyl methacrylate (DCTMA) monomer

Cyanuric chloride (6.6 g, 0.036 mol) was added to a stirred solution of 2-hydroxyethyl methacrylate (3.10 g, 0.024 mol) and *N,N*-diisopropylethylamine (6.27 ml, 0.036 mol) in THF (100 mL) at 0 °C for 3 hour. The solution was stirred in 16h at room temperature. The reaction solution was filtered to remove salt, then washed with distilled water three time and dried by K<sub>2</sub>CO<sub>3</sub>. The crude product was purified by flash chromatography over silica gel (n-heptane/EtOAc = 7/1) to yield 2-([4,6-dichlorotriazin-2-yl]oxy)ethyl methacrylate (DCTMA) (5.1 g, 0.018 mol, 76%) as a clear colorless oil. The monomer was

stored at -4 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 6.12 (d, 1H,  $=\text{CH}_2$  *cis*), 5.60 (d, 1H,  $=\text{CH}_2$  *trans*), 4.77 (t, 2H), 4.53 (t, 2H), 1.93 (s, 3H).

### Synthesis of 1-pyrenemethyl methacrylate (PMA) monomer

To the solution of triethylamine (1.80 ml, 12.8 mmol) in anhydrous THF (50 ml), pyrene-1-ylmethanol (1.0 g, 4.3 mmol) was added. Methacryloyl chloride (1.24 ml, 12.8 mmol) was added dropwise to this solution at 0 °C. The reaction was then stirred at room temperature overnight. Subsequently, the reaction was filtered and the solvent was evaporated under reduced pressure. Afterwards, the solid residue was dissolved in diethyl ether and washed with water several times. After evaporation of solvent, the crude monomer was purified via silica column and recrystallized from ethanol. The yield was 60%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.32-8.00 (m, 9H, aromatic), 6.16 (d, 1H,  $=\text{CH}_2$  *cis*), 5.91 (s, 2H), 5.57 (d, 1H,  $=\text{CH}_2$  *trans*), 1.98 (s, 3H).

### Synthesis of poly(3-hexylthiophene)-*block*-polymethacrylate (P3HT-*b*-PMA) copolymers

General procedure: P3HT-*b*-PMA was synthesized by UV light-induced metal-free ATRP using the P3HT-macroinitiator and pyrene/PPT<sub>h</sub> as photocatalyst. In a typical experiment, 0.1 g of P3HT-macroinitiator ( $M_n$  NMR = 9000 g mol<sup>-1</sup>, 0.011 mmol) was placed in a 25 mL flask, to which 3 mL of degassed THF was added by syringe. The P3HT-macroinitiator solution was stirred until it became homogeneous. A solution containing a methacrylate monomer and the photocatalyst was added separately. The mixture was degassed by three freeze-pump-thaw cycles. The solution was continuously stirred until it became homogeneous, and then placed in a UV-box (wavelength of 365 nm, with twelve lamps of 9 W circularly oriented) for 24 h at room temperature. Finally, the resultant polymer solution was precipitated into cold methanol, followed by drying under vacuum to give the desired product. Analysis of the extracted solvent after Soxhlet extraction of the product with acetone showed no PMMA homopolymer.

Poly(3-hexylthiophene)-*block*-poly(methyl methacrylate) (P3HT-*b*-PMMA, copolymer 8). FT-IR (cm<sup>-1</sup>): 724, 818, 1376, 1451, 1509, 1561, 1735, 2853, 2922, 2953.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 6.96 (s, 1H, P3HT), 3.60 (m, 3H, PMMA), 2.80 (t, 2H, P3HT), 2.00-1.69 (m, 2H, PMMA), 1.69 (quint, 2H, P3HT), 1.49-1.39 (m, 2H, P3HT), 1.39-1.28 (m, 4H, P3HT), 1.09-0.77 (m, 3H, PMMA), 0.89 (t, 3H, P3HT).

Poly(3-hexylthiophene)-*block*-poly(*N,N*-dimethylamino-2-ethyl methacrylate) (P3HT-*b*-PDMAEMA, copolymer 9). FT-IR (cm<sup>-1</sup>): 724, 818, 1376, 1451, 1509, 1561, 1735, 2853, 2922, 2953, 3056.  $^1\text{H}$  NMR

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(500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 6.96 (s, 1H, P3HT), 5.29 (s, 2H, iBu), 4.06 (s, 2H, PDMAEMA), 2.80 (t, 2H, P3HT), 2.58 (s, 2H, PDMAEMA), 2.28 (s, 6H, PDMAEMA), 2.05-1.78 (m, 2H, PDMAEMA), 1.93 (s, 6H, iBu), 1.69 (quint, 2H, P3HT), 1.49-1.39 (m, 2H, P3HT), 1.39-1.28 (m, 4H, P3HT), 1.12-0.80 (m, 3H, PDMAEMA), 0.89 (t, 3H, P3HT).

Poly(3-hexylthiophene)-*block*-poly(methyl methacrylate-*random*-pyrenemethyl methacrylate) (P3HT-*b*-P(MMA-*r*-PMA), copolymer 10). FT-IR ( $\text{cm}^{-1}$ ): 724, 818, 1376, 1451, 1509, 1561, 1735, 2853, 2922, 2953, 3056.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.04-8.17 (m, 9H, pyrene-H), 6.96 (s, 1H, P3HT), 5.73 (s, 2H, pyrenemethyl), 5.29 (s, 2H, iBu), 3.60 (m, 3H, PMMA), 2.80 (t, 2H, P3HT), 1.93 (s, 6H, iBu), 2.15-1.50 (m, 2H, PMA), 1.69 (quint, 2H, P3HT), 1.49-1.39 (m, 2H, P3HT), 1.39-1.28 (m, 4H, P3HT), 0.9-0.70 (m, 3H, PMA), 0.89 (t, 3H, P3HT).

Poly(3-hexylthiophene)-*block*-poly(2-([4,6-dichlorotriazin-2-yl]oxy)ethyl methacrylate) (P3HT-*b*-PDCTMA, copolymer 11). FT-IR ( $\text{cm}^{-1}$ ): 724, 818, 1376, 1451, 1509, 1561, 1735, 2853, 2922, 2953, 3056.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 6.98 (s, 1H, P3HT), 5.29 (s, 2H, iBu), 4.76 (s, 2H, PDCTMA), 4.37 (s, 2H, PDCTMA), 2.80 (t, 2H, P3HT), 1.93 (s, 6H, iBu), 1.9-1.60 (m, 2H, PDCTMA), 1.49-1.39 (m, 2H, P3HT), 1.39-1.28 (m, 4H, P3HT), 1.09-0.77 (m, 3H, PDCTMA), 0.89 (t, 3H, P3HT).

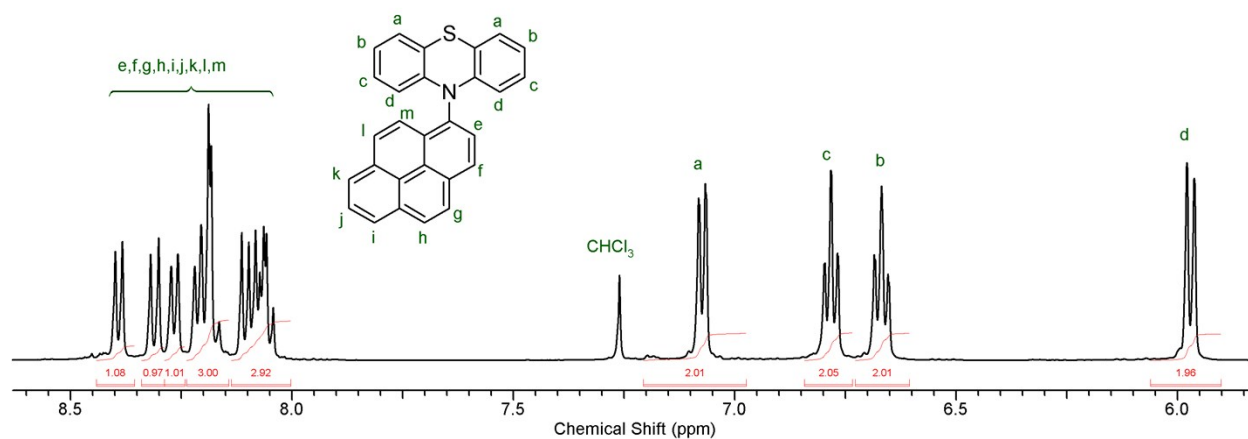


Fig. S1  $^1\text{H}$  NMR spectrum of 10-(pyren-1-yl)-10H-phenothiazine (PPTTh).

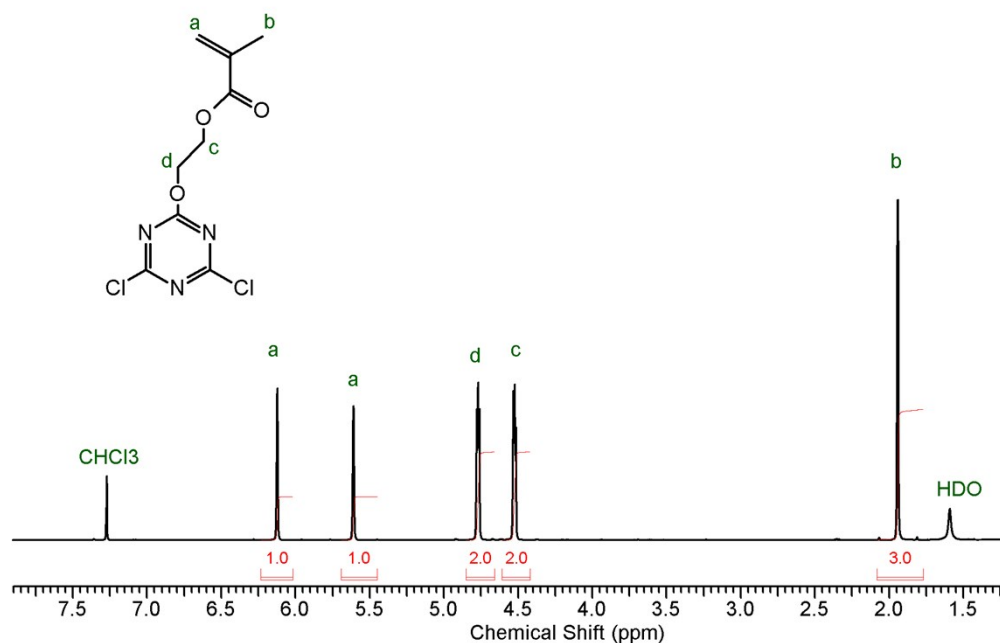


Fig. S2  $^1\text{H}$  NMR spectrum of 2-([4,6-dichlorotriazin-2-yl]oxy)ethyl methacrylate (DCTMA).

Table S1. Macromolecular characteristic features of homopolymers synthesized by metal-free ATRP of methyl methacrylate (MMA) and *N,N*-dimethylamino-2-ethyl methacrylate (DMAEMA) in THF using PPT<sub>h</sub> as photocatalyst and ethyl 2-bromo-2-methylpropanoate (EBMP) as initiator under UV irradiation at room temperature for 24 h

Entry	Monomer	[Monomer] <sub>0</sub> /[EBMP]/[PPT <sub>h</sub> ]	Conv <sup>a</sup> (%)	$M_{n,\text{GPC}}^b$ (g mol <sup>-1</sup> )	$\bar{D}^b$
1	MMA	100/1/0.05	24	4300	1.14
2	MMA	100/1/0.1	85	9000	1.12
3	MMA	100/1/0.5	60	7600	1.25
4	MMA	100/1/1	55	7200	1.40
5	DMAEMA	100/1/0.05	38	6700	1.15
6	DMAEMA	100/1/0.1	96	14700	1.18
7	DMAEMA	100/1/0.5	78	9900	1.17
8	DMAEMA	100/1/1	60	8000	1.23

<sup>a</sup> Conversion as determined gravimetrically:  $\text{Conv} = (m - m_i - m_{\text{PC}})/m_{\text{M}}$  where  $m$  denotes the weight of product, and  $m_i$ ,  $m_{\text{PC}}$  and  $m_{\text{M}}$  the weights of the macroinitiator, photocatalyst and monomer, respectively.

<sup>b</sup> Determined by GPC in THF using polystyrene standards.



Table S2. Macromolecular characteristic features of diblock copolymers as obtained from P3HT-macroinitiator ( $M_{n,NMR} = 9000 \text{ g mol}^{-1}$ ,  $M_{n,GPC} = 8100 \text{ g mol}^{-1}$ ,  $\bar{D} = 1.18$ ) by metal-free ATRP processes of DMAEMA in THF using pyrene and PPTH as organic photocatalysts under different light sources at room temperature for 24 h

Entry	PC	[Monomer] <sub>0</sub> /[P3HT- iBuBr]/[PC]	Wavelength	Light intensity (mW/cm <sup>2</sup> )	Conv <sup>a</sup> (%)	PDMAEMA block	P3HT- <i>b</i> -PDMAEMA	
						$M_{n,theo}^b$ (g mol <sup>-1</sup> )	$M_{n,GPC}$ (g mol <sup>-1</sup> )	$\bar{D}$
1	Pyrene	60/1/1	365	2.2	91	8584	19700	1.24
2	Pyrene	60/1/1	365	0.05	31	2924	13100	1.22
3	Pyrene	60/1/1	465	0.06	2	189	8200	1.18
4	PPTH	60/1/0.1	365	2.2	93	8772	21000	1.24
5	PPTH	60/1/0.1	365	0.05	35	3300	14000	1.20
6	PPTH	60/1/0.1	465	0.06	23	2170	12700	1.20

<sup>a</sup> Conversion as determined gravimetrically:  $\text{Conv} = (m - m_i - m_{PC})/m_M$  where  $m$  denotes the weight of product, and  $m_i$ ,  $m_{PC}$  and  $m_M$  the weights of the macroinitiator, photocatalyst and monomer, respectively

<sup>b</sup> Theoretical number-average molar mass of the coil block as calculated by  $[\text{Monomer}]_0/[\text{P3HT-iBuBr}] \times \text{Conv} \times M_{w \text{ monomer}}$  assuming a living/controlled process