Supporting Information

Single Chain Self-Assembly: Preparation of α,ω-Donor-Acceptor Chains via Living Radical Polymerization and Orthogonal Conjugation

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Materials and Instrumentation

Styrene (Sigma-Aldrich) was passed through a column of basic alumina (Acros) prior to use. 6-Bromohexanol (97%, ABCR GmbH and Co. KG), cyanuric acid (99%, ABCR GmbH and Co. KG), 4-dimethylamino pyridine (DMAP) (99%, Acros), N,N-dicyclohexylcarbodiimide (DCC) (99%, Acros), N,N-dimethylformamide extra dry (DMF) (99.8%, Acros), tetrahydrofuran extra dry (THF) (99.8%, Acros), sodium azide (99.8%, Acros), α-bromo isobutyric acid (Aldrich), 5-hydroxyisophthalic acid (97%, Aldrich), sulfuric acid (95%, Carl Roth GmbH and Co. KG), propargyl bromide, 80 wt.% solution in toluene (Acros), trimethyl acetyl chloride (99%, Aldrich), 2,6-diamino pyridine (98%, Aldrich), triethylamine (99%, Acros), CuBr (99.9%, Acros) N,N,N',N'',N'-pentamethyl diethyl triamine (PMDETA) (Merck), cupric sulfate pentahydrate (99.5%, BDH), (+)-sodium L-ascorbate (98%, Sigma) were used as received. Dichloromethane (DCM) was distilled over phosphorus pentoxide and stored over molecular sieves. Toluene, diethyl ether, ethanol, methanol and chloroform were purchased as analytical grade and used as received.

Size Exclusion Chromatography (SEC)

SEC measurements were performed on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 μm bead-size guard column (50 × 7.5 mm) followed by three PLgel 5 μm Mixed-C and one PLgel 3 μm Mixed-E columns (300 × 7.5 mm) and a differential refractive index detector using THF as the eluent at 40 °C with a flow rate of 1 $\mathrm{mL \cdot min^{-1}}$. The SEC system was calibrated using linear poly(styrene) (PS) standards ranging from 160 to $6 \cdot 10^{6}$ g $\mathrm{mol^{-1}}$. Calculation of the molecular weight proceeded via the Mark-Houwink parameters for this polymer, i.e. $K = 14.1 \cdot 10^{-5}$ $\mathrm{dL \cdot g^{-1}}$, $\alpha = 0.70$ (PS).[1]

Attenuated Total Reflectance-Infra Red Spectroscopy (ATR-IR)

Solid-state Fourier transform infrared spectra were recorded with an attenuated total reflectance unit (Bruker, *Golden Gate*) coupled to a Bruker Vertex 80 Fourier-transform spectrometer, equipped with a tungsten halogen lamp, a KBr beam splitter and DTGS detector.

Electrospray Ionization-Mass Spectrometry (ESI-MS) Measurements

Mass spectra were recorded on an LXQ mass spectrometer (ThermoFisher Scientific, San Jose, CA, USA) equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The instrument was calibrated in the m/z range 195-1822 using a standard containing caffeine, Met-Arg-Phe-Ala acetate (MRFA) and a mixture of fluorinated phosphazenes (Ultramark 1621) (all from Aldrich). A constant spray voltage of 3.5 kV and a dimensionless sheath gas of 8 and a sweep gas flow rate of 2 were applied. The capillary voltage, the tube lens offset voltage, and the capillary temperature, were set to 60 V, 120 V and 275 °C, respectively.

Nuclear Magnetic Resonance (NMR) Spectroscopy Measurements

The structures of the synthesized compounds were confirmed by ^{1}H-NMR and ^{13}C-NMR spectroscopy using a Bruker AM 400 MHz spectrometer for hydrogen nuclei and 100 MHz for carbon nuclei. Samples were dissolved in $CDCl_3$ or DMSO-d_6. The δ–scale is referenced to tetramethylsilane (δ = 0.00) as internal standard.

Dynamic Light Scattering (DLS) Measurements

Hydrodynamic radii and diameter values were determined using a Nicomp submicron particle sizer model 380 DLS (Polymer Sizing Systems, Santa Barbara, CA) which works on the principle of photon correlation spectroscopy. The Nicomp 380 DLS is equipped with an avalange photo detector with high sensitivity for small particles and a laser diode (90 mW, 658 nm). Dynamic light scattering data were collected in the drop-in cell mode. All measurements were determined at 90° to the incident beam.

Synthesis

5-(prop-2-ynyloxy)isophthaloyl dichloride[2] (**1**) and N-(6-aminopyridin-2-yl)pivalamide[3] (**2**) were synthesized according to the literatures.

N^1, N^3-bis(6-pivalamidopyridin-2-yl)-5-(prop-2-ynyloxy)isophthalamide (3): A solution of compound **1** (1 g, 3.89 mmol) in dry THF (20 mL) was added dropwise to a solution of compound **2** (1.8 g, 9.33 mmol) and triethylamine (1.62 mL, 11.67 mmol) in dry THF (20 mL) at 0 ^{o}C. The solution was stirred at ambient temperature for 12 h, the residue filtered off and the solvent removed under reduced pressure. Purification by column chromatography on silica gel (CH_2Cl_2/ethyl acetate (4:1) as eluent) gave a white solid. (1.62 g, 73%). ^{1}H NMR (400 Hz, DMSO-d$_6$) ∂ 1.25 (s, 18H), 3.36 (s, 1H), 5.01 (s, 2H), 7.78-7.9 (m, 8H), 8.23 (s, 1H), 9.29 (s, 2H), 10.59 (s, 2H). ^{13}C NMR (100 Hz, DMSO-d$_6$) ∂ 28.0, 39.4, 57.0, 76.4, 78.8, 105.2, 115.1, 117.4, 135.3, 141.0, 149.1, 156.3, 160.9, 164.8, 176.8 MS-ESI $(M+Na)^+$ calcd for $C_{31}H_{34}N_6O_5$: 593.25, found 593.37 (Figure 1S and Figure S2).

1-(6-hydroxyhexyl)-1,3,5-triazinane-2,4,6-trione (4): Compound **4** was synthesized by modification of the method provided in ref.[4]. 6-Bromohexan-1-ol (1.81 g, 10 mmol) and cyanuric acid (6.50 g, 50 mmol) were dissolved in dry DMF (50 mL). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 1.5 mL, 10 mmol) was added dropwise to the solution. The mixture was heated to 70 ^{o}C and stirred for 24 h. The solvent was evaporated and the crude mixture was dissolved with methanol and filtered. The solvent was evaporated off and the residual purified via chromatography on silica gel, eluting with CH_2Cl_2/CH_3OH (4:1) to obtain compound **4** as a white solid (1.35 g, 59%). %). ^{1}H NMR (400 Hz, DMSO-d$_6$)

∂ 1.26 (m, 4H), 1.39 (m, 2H), 1.49 (m, 2H), 3.36-3.35 (t, 2H), 3.58.3.64 (t, 2H), 4.35 (brs, 1H), 11.37 (brs, 2H). ^{13}C NMR (100 Hz, DMSO-d$_6$) 28.52, 30.40, 32.50, 33.45, 45.60, 62.64, 72.23, 153.85, 155.13, 175.99 (Figure 3S).

6-(2,4,6-trioxo-1,3,5-triazinan-1-yl)hexyl 2-bromo-2-methylpropanoate (5): Precursor **4** (1 g, 4.36 mmol) was dissolved in 5 mL dry (DMF). 2-Bromo-2-methyl propionic acid (0.947 g, 5.67 mmol) and 4-dimethylaminopyridine (DMAP) (0.069 g, 0.56 mmol) were dissolved in 10 mL dry DCM and subsequently added to the mixture. DCC (1.75 g, 8.5 mmol) was dissolved in 5 mL dry DCM and then added to the solution at 0 ^{o}C. The reaction was carried out at ambient temperature overnight. Solids were filtered off, the filtrate was concentrated and the crude product was purified by column chromatography on silica gel, eluting with CH_2Cl_2/MeOH (25/1) to give the ATRP initiator as a white solid (0.615 g, 37%). ^{1}H NMR (400 Hz, DMSO-d$_6$) ∂ 1.26 (m, 4H), 1.39 (m, 2H), 1.49 (m, 2H), 1.86 (s, 6H), 3.58-3.64 (t, 2H), 4.07-4.12 (t, 2H), 11.37 (brs, 2H). ^{13}C NMR (100 Hz, DMSO-d$_6$) 28.52, 30.40, 32.50, 33.45, 45.60, 72.23, 153.85, 155.13 MS-ESI (M+Na)$^+$ calcd for $C_{13}H_{20}BrN_3O_5$: 400.05, found 400.08 (Figure 4S).

Synthesis of α-cyanuric acid functional polystyrene (6): Into a 50 mL of Schlenk tube, styrene (6.0 mL, 52.89 mmol), PMDETA (0.063 mL, 0.264 mmol), CuBr (0.038 g, 0.264 mmol), and **5** (0.1 g, 0.264 mmol) in 0.6 mL of anisole were added and the reaction mixture was degassed by three freeze-pump-thaw cycles and left under argon. The tube was subsequently placed in a thermostatted oil bath at 90 ^{o}C for 90 min. The polymerization mixture was diluted with THF, passed through an alumina column to remove the catalyst, and precipitated in methanol. The polymer was dried for 24 h in a vacuum oven at 25 ^{o}C to give a white solid (0.6 g) Yield: 11%. ^{1}H NMR (400 Hz, $CDCl_3$) ∂ 7.98 (s, 2H of cyanuric acid), 7.01-6.39 (5H, Ar*H* of PS), 4.42-4.33 (1H, C*H*Br), 3.73 (2H, CH_2-N), 3.45(2H, CH_2-O), 1.78-1.18 (aliphatic protons of PS), 0.90-077 (6H, $NCH_2(CH_2)_3CH_2O$). $M_{n,NMR}$ = 5500 Da, $M_{n,SEC}$ =

5000 Da, *PDI* = 1.04. The integral areas of the N-*H* bond of the cyanuric acid signal and that of the C*H*-Br of PS in the corresponding ^{1}H NMR spectrum have been compared and the bromo functionality of polymer **6** has been determined as being close to 96% relative to cyanuric acid termini.

Synthesis of α-cyanuric acid functional polystyrene with azide (7): The bromide of polystyrene (**6**) was converted to the azide functionality following the literature.[5] Yield: 96%. FTIR (cm^{-1}): 2095 (N_3 stretching). $M_{n,NMR}$ = 5400 Da, $M_{n,SEC}$ = 5000 Da, *PDI* = 1.04. After the reaction with sodium azide the C*H*-Br disappears completely, indicating ~100% transformation.

Synthesis of α,ω-donor-acceptor single chain polystyrene (8): Compound **7** (0.2 g, 0.036 mmol), compound **3** (41.98 mg, 0.073 mmol), copper (II) sulfate pentahydrate (17.63 mg, 0.11 mmol) and sodium ascorbate (21.89 mg, 0.11 mmol) were dissolved in DMF (5 mL). The resulting mixture was stirred at ambient temperature for 24 h before the copper catalyst was removed by passage through a short column of neutral alumina. The solvent was removed under reduced pressure and subsequently diluted with the addition of THF. The polymer was precipitated in 100 mL of methanol, filtered and dried under vacuum at 25 °C for 24 h to obtain a white solid (0.238 g) Yield: 98%. ^{1}H NMR (400 Hz, $CDCl_3$) ∂ 7.96-7.76 (9H, ArH of host), 7.01-6.39 (5H, Ar*H* of PS), 5.13-5.03 (2H, OCH_2 linked to triazole), 3.73 (2H, CH_2-N), 3.45(2H, CH_2-O), 1.78-1.18 (aliphatic protons of PS), 0.90-077 (6H, $NCH_2(CH_2)_3CH_2O$). $M_{n,NMR}$ = 6000 Da, $M_{n,SEC}$ = 6100 Da, *PDI* = 1.04

Self-assembly studies between polymer 6 and compound 3: Six different samples were prepared with dissolved polymer **6** (21.9 mg) in 1 mL $CDCl_3$ in an NMR tube. The concentration of **6** was kept constant at 4 mM. Compound **3** was added to the each solution in

1, 2, 3, 4, and 5 equiv., respectively. The mixtures were left to assemble overnight (12 h) at ambient temperature; subsequently ^{1}H NMR spectra were recorded (Figure 1C).

Single chain self-assembly studies of polymer 8 with ^{1}H NMR: 6.0 mg, 12.0 mg, and 24.0 mg of the polymer **8** were dissolved in 1 mL $CDCl_3$ in an NMR tube and left to assemble overnight (12 h); ^{1}H NMR spectra were subsequently recorded (Figure 3).

Single chain self-assembly studies of polymer 8 via DLS: Solutions of **8** were prepared by dissolving 3.0 mg, 4.5 mg, 6.0 mg, 9.0 mg, 12.0 mg, and 18.0 mg of the polymer **8** in 1 mL $CHCl_3$ to obtain six concentrations. A few solutions of polystyrene standards were also prepared in a similar fashion (see Table S1). Solvents and polymer solutions were filtered through 0.2 μm and 0.5 μm PTFE filters, respectively, and measured after 12 h assembly at ambient temperature in the scattering cell (see Figure 4 and Table S1). One polystyrene (PS) standard (9100 Da) was measured in several concentrations showing no measurable difference in hydrodynamic diameter D_h (see Table S1). Such an observation confirms that one can neglect the influence of concentration and the scattering angle on the diffusion coefficient and consequently also on the hydrodynamic radii R_h for the molecule sizes and concentrations in our experiments. Thus, any change in D_h as a function of concentrations observed with polymer **8** is a result of the hydrogen-bonding associations. The constant values of D_h at lower concentrations of **8** clearly indicate that the smallest possible folding has occurred, i.e. the circular self-assembly of a single chain of **8**.

The theoretical values provided in Table 1 are calculated as follows. Starting from the Einstein equation of viscosity, it follows that: $[\eta]\cdot M_n = ((10\cdot\pi\cdot N_A)/3)\cdot R_h^3$ or $R_h = ([\eta]\cdot M_n\cdot 3/(10\cdot\pi\cdot N_A))^{1/3}$ with $D_h = 2\cdot R_h$, where $[\eta]$ is the intrinsic viscosity, M_n the number average molecular weight and N_A = Avogrado's constant. For the calculation of $[\eta]$ Mark-Houwink parameters K_η and α_η from the Polymer Handbook were employed[6] (two values for polystyrene in chloroform at 25 °C were employed [$K_\eta^1 = 7.2\cdot10^{-5}$ dL g^{-1}, $\alpha_\eta^1 = 0.76$ and $K_\eta^2 = 11.2\cdot10^{-5}$ dL g^{-1}, $\alpha_\eta^2 = 0.73$]) and the resulting R_h values averaged.

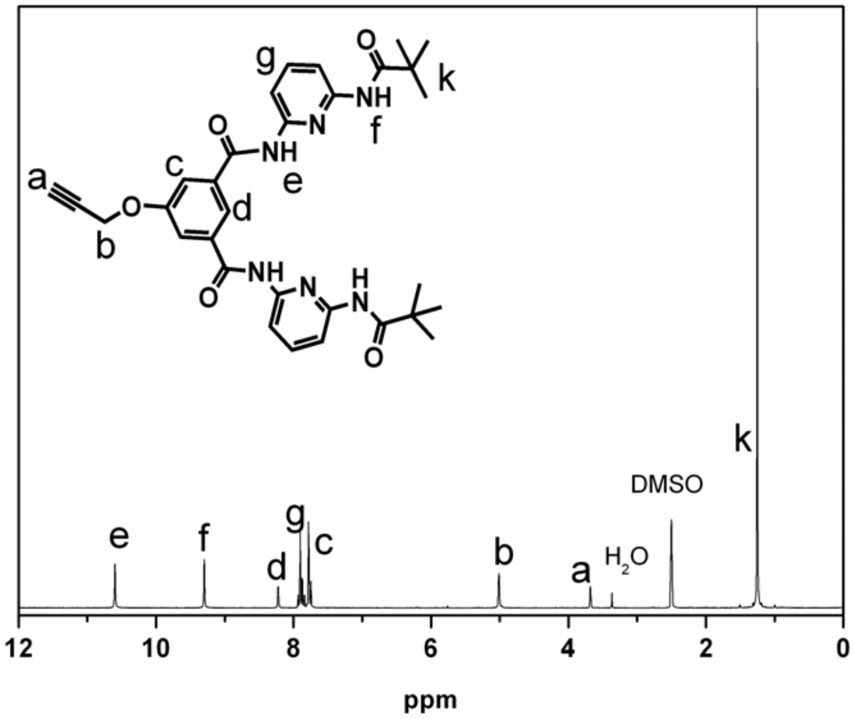

Figure S1. ^{1}H NMR of compound **3** in DMSO-d_6

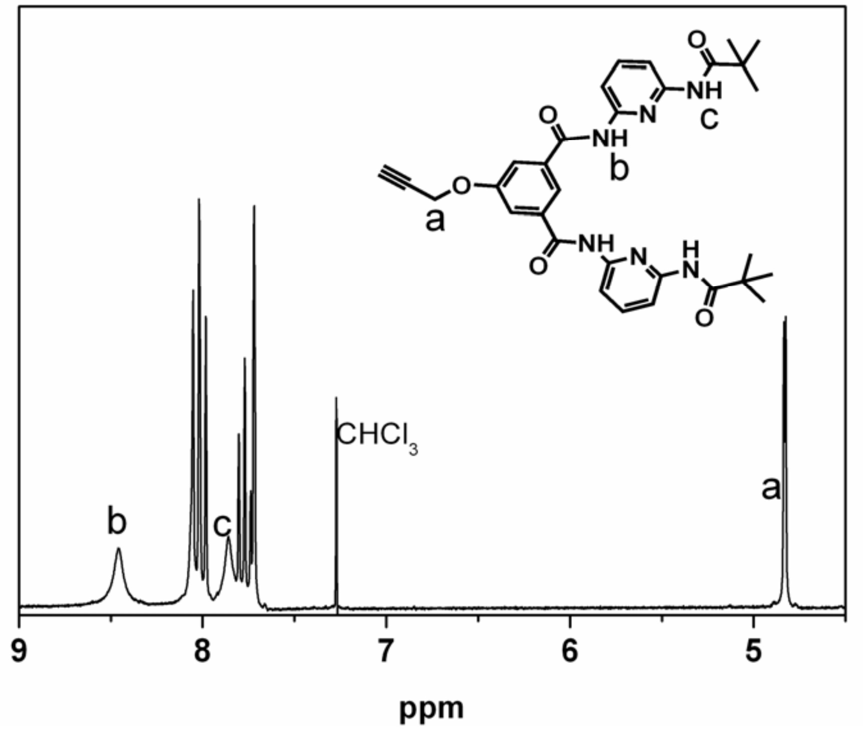

Figure S2. Zoomed ^{1}H NMR of compound **3** in CDCl$_3$

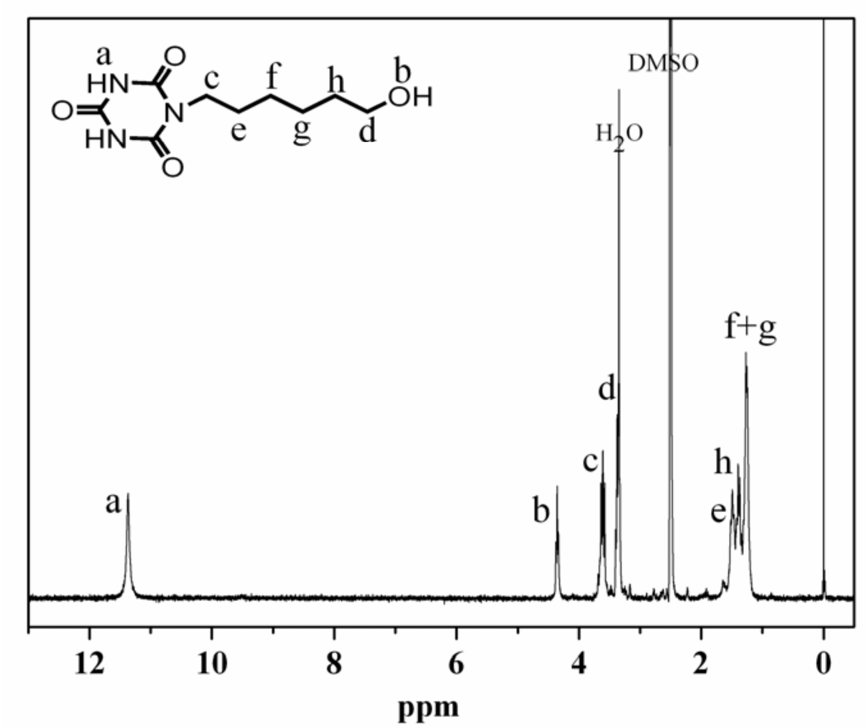

Figure S3. ^{1}H NMR of compound **4** in DMSO-d_6

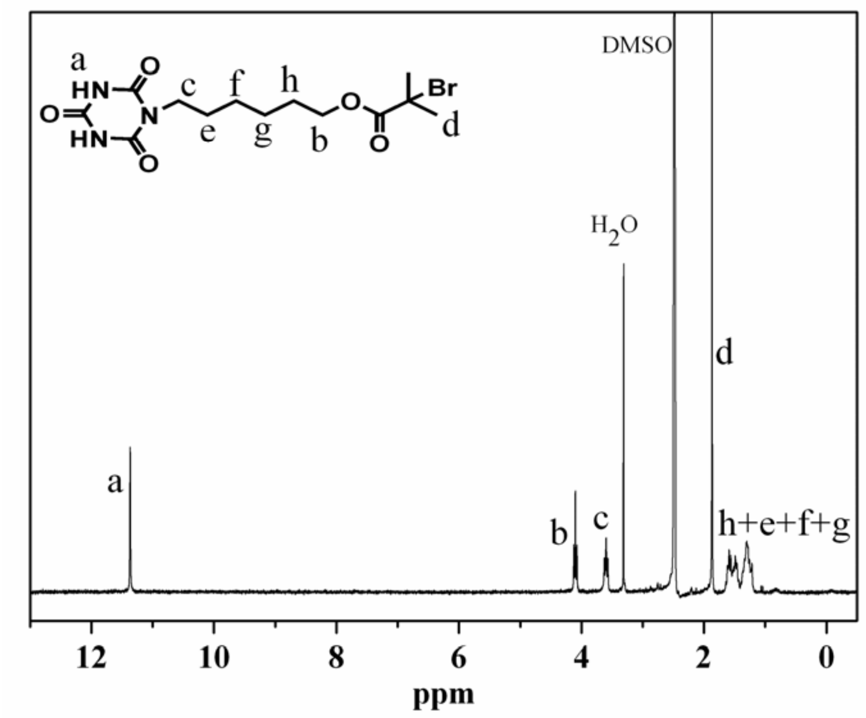

Figure S4. ^{1}H NMR of compound **5** in DMSO-d_6

Table S1. Hydrodynamic diameter, D_h, of the polymer **8** in different concentrations as well as polystyrene standards in $CHCl_3$ at 25 °C.

Polymer	D_h^{exp} / nm	D_h^{theo} / nm[6]
1 mM PS-standard (M_n=9100 Da)	4.6	4.6
2 mM PS-standard (M_n=9100 Da)	4.6	4.6
3 mM PS-standard (M_n=9100 Da)	4.6	4.6
10 mM PS-standard (M_n=3400 Da)	2.4	2.4
3 mM of **8**	5.0	
2 mM of **8**	5.0	
1.5 mM of **8**	4.6	
1 mM of **8**	4.3	
0.75 mM of **8**	4.1	
0.5 mM of **8**	4.1	

References and Notes

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[S-6] The Mark-Houwink parameter for the calculation of [η] has been taken from: I. Brandrup, E. Immergut, *Polymer Handbook*, Wiley & Sons 4th edition, New York, **2003**.