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Supporting Information for:

Copper-free click chemistry for the *in situ* crosslinking of photodegradable star polymers

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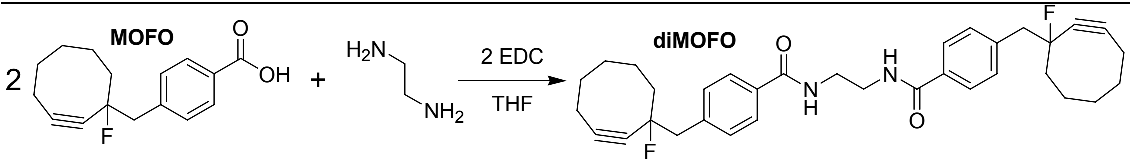
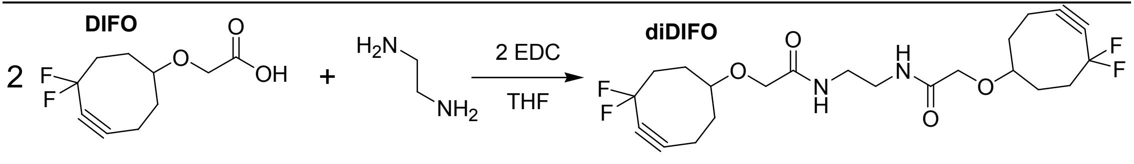
General. All reagents were purchased from Aldrich chemical company and were used as supplied unless otherwise noted. Star polymer **1**, **MOFO**, and **DIFO** were prepared following literature procedures.[1,2,3] SEC measurements were performed on a Knauer GPC system with a Knauer K-2301 refractive index detector and a Spark Holland Basic Marathon autosampler. Three Polymer Laboratories 5 μm particle size PLgel columns (one 100 Å and two MIXED-D pore types) placed in series were employed for the chromatography. The system was calibrated against linear polystyrene standards ranging in molecular weight from 580-377,400 Da. Experiments were performed at room temperature in THF eluant with a flow rate of 1.0 mL/min. Fourier transform infrared spectroscopy (FTIR) was performed using a Nicolet Nexus 870 FTIR system with a Harrick solution cell consisting of two 13 X 2 mm diameter CaF_2 plates with a 25 μm Teflon spacer. FTIR data was analyzed using OMNIC version 7.1a software from Thermo-Nicolet Corporation. Gel samples were degraded by UV irradiation using a Rayonet RPR-100 reactor from the Southern New England Ultraviolet Company fitted with RPR-3500 lamps (350 nm peak wavelength).



Synthesis of diMOFO. **MOFO** (46 mg, 0.18 mmol) was dissolved in THF (10 mL) in a dry round-bottom flask and cooled to 0 °C under argon atmosphere. *N*-(3-dimethylaminopropyl)-*N’*-ethylcarbodiimide hydrochloride (33.9 mg, 0.18 mmol) and 1-hydroxybenzotriazole (23.9 mg, 0.18 mmol) were then added and the suspension was stirred at 0 °C for 10 min before the dropwise addition of ethylene diamine (5.3 mg, 0.088 mmol). Upon addition of ethylene diamine the suspension immediately became cloudier. After stirring at 0 °C for 30 min, the mixture was warmed to room temperature and stirred for 4 h after which time the contents of the flask were filtered, concentrated on a rotary evaporator, diluted with ethyl acetate, and washed with 1.0 M HCl (2 X 10 mL), saturated $NaHCO_3$ (2 X 10 mL), and brine (1 X 10 mL). The organic layer was then dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography (75% ethyl acetate:hexanes, R_f = 0.3, anisaldehyde stain for TLC plates) to yield **diMOFO** (45.1 mg, 94%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (d, 4 H, *J* = 8.1 Hz), 7.41 (br, 2 h), 7.34 (d, 4 H, *J* = 8.1 Hz), 3.65 (s, 4 H), 3.04 (d, 4 H, J = 20.6 Hz), 2.21 (m, 4 H), 1.89 (m, 8 H), 1.71 (m, 4 H), 1.34 (m, 4 H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 168.93, 140.10, 132.61, 130.76, 127.12, 104.88, 104.75, 96.72, 94.39, 91.03, 90.63, 48.21, 47.90, 45.02, 44.71, 41.14, 34.28, 29.64, 26.92, 20.73; IR (cm^{-1}) 3307, 2926, 2842, 2224, 1630, 1537, 1504, 1444, 1290; APCI$^+$ LRMS calcd. for $C_{34}H_{38}F_2N_2O_2$ $[M+H]^+$ 545.3, found 545.0.



Synthesis of diDIFO. **DIFO** (10 mg, 0.046 mmol) was dissolved in THF (4 mL) in a dry round-bottom flask and cooled to 0 °C under argon atmosphere. *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (8.8 mg, 0.046 mmol) was added and the suspension was stirred at 0 °C for 10 min before the dropwise addition of ethylene diamine (1.4 mg, 0.023 mmol). As for the synthesis of **diMOFO** above, upon addition of ethylene diamine the suspension immediately became cloudier. After stirring at 0 °C for 30 min, the mixture was warmed to room temperature and stirred overnight (monitored by TLC, 5% methanol:dichloromethane, R_f = 0.4) after which time the contents of the flask were filtered, concentrated on a rotary evaporator, diluted with ethyl acetate, and washed with 1.0 M HCl (2 X 10 mL), saturated $NaHCO_3$ (2 X 10 mL), and brine (1 X 10 mL). The organic layer was then dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography (2% methanol in methylene chloride, R_f = 0.4, anisaldehyde stain for TLC plates) to yield **diDIFO** (6.2 mg, 59%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (br, 2 H), 3.93 (d, 4 H, *J* = 3.3 Hz), 3.52 (br, 2 H), 3.48 (s, 4 H), 2.56 (m, 4 H), 2.46 (m, 4 H), 2.26 (m, 4 H), 2.06 (m, 4 H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 170.85, 110.94, 83.63, 81.91, 75.78, 68.39, 39.86, 39.05, 33.82, 30.14, 17.56: δ ; IR (cm^{-1}) 3422, 2917, 2849, 2219, 1668, 1539, 1436, 1129, 1104, 1026, 737; APCI$^+$ LRMS calcd. for $C_{22}H_{28}F_2N_2O_4$ $[M]^+$ 460.2, found 460.3.

References:

1. Johnson, J. A.; Finn, M. G.; Koberstein, J. T.; Turro, N. J., *Macromolecules* **2007**, *40*, 3589-3598.
2. Agard, N. J.; Baskin, J. M.; Prescher, J. A.; Lo, A.; Bertozzi, C. R., *ACS Chem. Biol.* **2006**, *1*, 644-648.
3. Baskin, J. M.; Prescher, J. A.; Laughlin, S. T.; Agard, N. J.; Chang, P. V.; Miller, I. A.; Lo, A.; Codelli, J. A.; Bertozzi, C. R. *Proc. Natl. Acad. Sci. U.S.A.*, 2007, **104**, 16793.