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Electronic Supplementary Information

Rigidity-Induced Emission Enhancement of Network Polymers Crosslinked by Tetraphenylethene Derivatives

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Experimental section

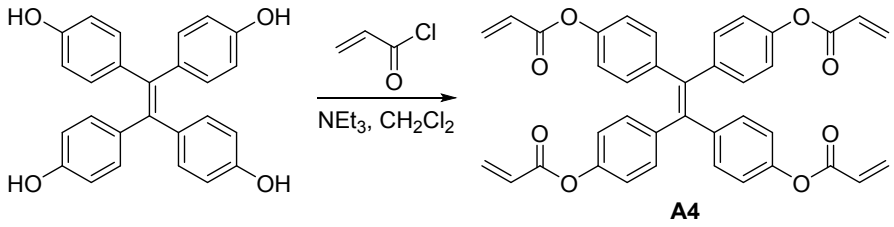
Materials

Unless stated otherwise, all other reagents were obtained from commercial sources and used without further purification. Tetra(4-hydroxyphenyl)ethene was synthesized and characterized according to the reported method.[1] The reaction was carried out under nitrogen atmosphere.

Measurements

^{1}H (500 MHz) and ^{13}C (126 MHz) NMR measurements were recorded on a Bruker Biospin AVANCE DRX500 instrument, using 0.05% tetramethylsilane (TMS) as an internal standard. UV–Vis spectra were recorded on a JASCO V-570 spectrophotometer at room temperature. Emission spectra were obtained with SHIMADZU RF5300PC spectrofluorometer. Temperature dependent emission spectra were observed with a JASCO FP-6600 spectrofluorometer, and the sample temperature was controlled by a JASCO ETC-273 Peltier-type temperature controller. The absolute luminescence quantum yield (Φ_F) was measured by a Hamamatsu C9920-02 absolute photoluminescence quantum yield measurement system equipped with an integrating sphere apparatus and a 150W continuous-wave xenon light source. Fourier transform infrared (FTIR) spectra were observed with a JASCO FTIR-4100 SK spectrometer with a ZnSe prism kit PKS-ZNSE

for ATR technique. Tensile test was carried out by an Instron 5965 5kN Dual Column Tabletop Universal Testing System with a 10 mm/min of tension rate. Differential Scanning Calorimetry (DSC) was conducted by METLLER TOLEDO DSC1 Star System with heating rate of 10 °C /min under nitrogen atmosphere.



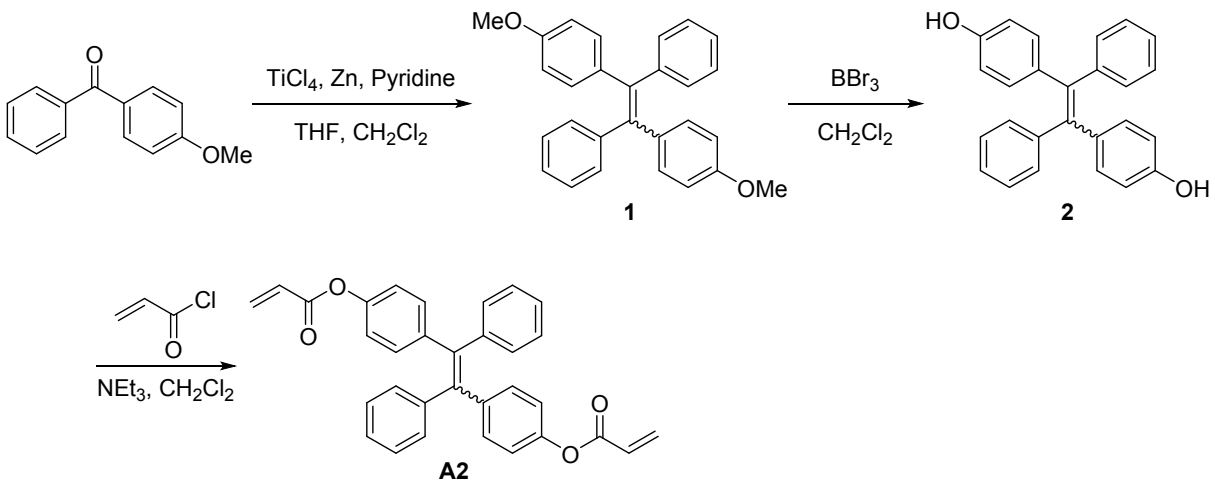
Scheme S1. Synthetic route for acryloyl compound **A4**.

Synthesis of tetra(4-acryloxyphenyl)ethene (A4)

In a 50 mL two-necked flask, tetra(4-hydroxyphenyl)ethene (513 mg, 1.29 mmol) was dissolved in anhydrous dichloromethane (10 mL) and stirred for 20 min in ice salt bath. To the solution was added triethylamine (917 mg, 9.06 mmol 7.00 eq.), then acryloyl chloride (825 mg, 9.12 mmol 7.05 eq) was added dropwise. After stirring for 24 h at room temperature, the mixture was washed with saturated aqueous sodium hydrogen carbonate and distilled water. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography ($CHCl_3$/MeOH = 50/1) to afford **A4** as a pale yellow solid (361 mg, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.05 (8H, d, J = 8.65 Hz), 6.92 (8H, d, J = 8.6

Hz), 6.57 (4H, dd, J = 17.3, 1.1 Hz), 6.28 (4H, dd, J = 17.3, 10.5 Hz), 5.99 (4H, dd, J = 10.5, 1.1 Hz).

HRMS (EI): m/z calcd. for $C_{38}H_{28}O_8$: 612.17842 $[M]^+$, found: 612.17709 $[M]^+$.



Scheme S2. Synthetic route for acryloyl compound **A2**.

Synthesis of 1,2-di(4-methoxyphenyl)-1,2-diphenylethene (1)

In a 300 mL three-necked flask, zinc powder (2.64 g, 40.4 mmol 2.1 eq.) was dissolved in anhydrous THF (30 mL) and pyridine (1.5 mL, 18.4 mmol). After cooling to 0 °C, 1.0 M $TiCl_4$ solution in CH_2Cl_2 (20 mL, 20.0 mmol 1.1 eq.) and p-methoxybenzophenone (4.01 g, 18.9 mmol) dissolved in anhydrous THF (40 mL) and anhydrous CH_2Cl_2 (40 mL) added dropwise, and the mixture was refluxed for 20 h. The reaction mixture was cooled to room temperature, and 5% aqueous potassium carbonate was added. Then the mixture was filtered off, and THF was removed under reduced pressure. The residue was extracted with CH_2Cl_2, and the organic layer was dried

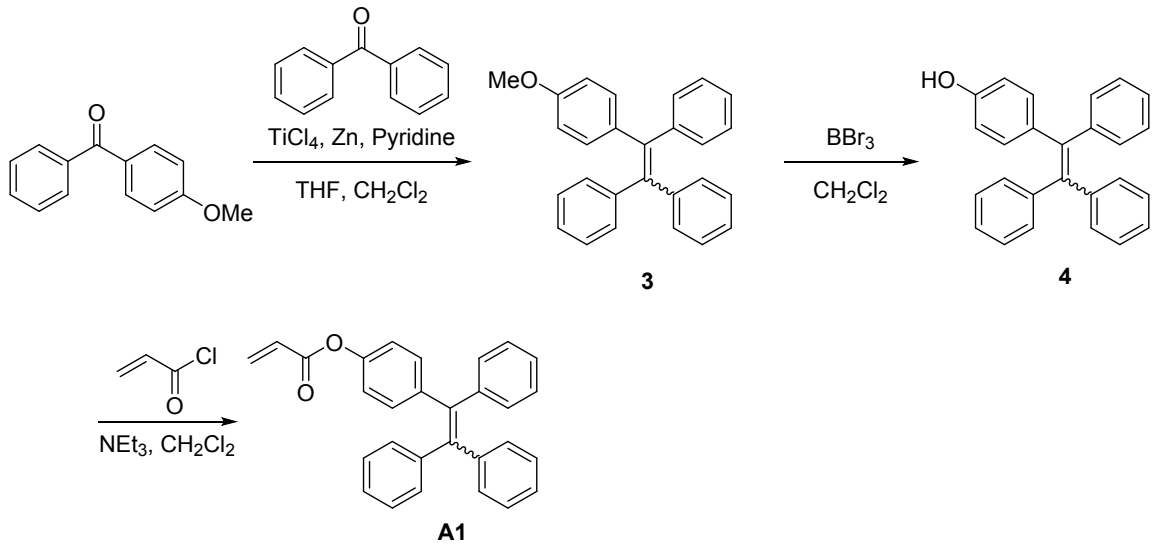
over $MgSO_4$. After removal of the solvent, the residue was purified by silica gel column chromatography ($CHCl_3$/hexane = 1/1) to obtain **1** as a yellow solid (3.11 g, 84%). ^{1}H NMR (500 MHz, CDCl3) δ (ppm) 7.17-7.00 (10H, m), 6.93 (4H, dd, J = 16.7, 8.7 Hz), 6.64 (4H, dd, J = 16.2, 8.7 Hz), 3.74 (6H, s).

Synthesis of 1,2-di(4-hydroxyphenyl)-1,2-diphenylethene (2)

In a 300 mL three-necked flask, anhydrous CH_2Cl_2 was added to dissolve **1** (1.20 g, 3.06 mmol), and cooled in ice-salt bath. To the solution was dropwise added 1.0 M BBr3 in CH_2Cl_2 (12 mL, 12 mmol), and stirred for 30 min at 0 °C. After warming to room temperature, the mixture was stirred for 22 h. Then distilled water (20 mL) was added to the mixture, and it was stirred additional 2 h. The mixture was extracted with CH_2Cl_2, and the organic layer was dried over Na_2SO_4. After removal of the solvent, compound **2** was obtained as white solid (1.14 g, 97%). 1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.13-6.99 (10H, m), 6.88 (dd, 15.7, 8.7 Hz), 6.57 (4H, dd, J = 16.5, 8.7 Hz), 4.58 and 4.55 (2H, s).

Synthesis of 1,2-di(4-acryl0xyphenyl)-1,2-diphenylethene(A2)

In a 300 mL two-necked flask, compound **2** was dissolved in anhydrous CH_2Cl_2 (15 mL), and triethylamine (238.5 mg, 2.36 mmol) was added to the solution. Then, acryloyl chloride (212.2 mg, 2.34 mmol) was added dropwise to the solution, and the mixture was stirred for 24 h at room temperature. The reaction mixture was washed with saturated aqueous sodium hydrogen carbonate and distilled water. The organic layer was dried over Na_2SO_4, and following removal of the solvent gave **A2** as a yellow solid (280 mg. 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.14-7.01 (14H, m), 6.92-6.87 (4H, m), 6.59-6.54 (2H, m), 6.31-6.24 (2H, m), 6.00-5.96 (2H, m).



Scheme S3. Synthetic route for acryloyl compound **A1**.

Synthesis of 1-methoxy-4-(1,2,2-triphenylethynyl)benzene (3)

In a 300 mL three-necked flask was placed zinc powder (2.03 g, 31.0 mmol), and anhydrous THF (50 mL) and pyridine (11.15 g, 14.6 mmol) was added. At 0 °C, 1.0 M $TiCl_4$ in CH_2Cl_2 (15 mL, 15 mmol) was added to the mixture, and *p*-methoxybenzophenone (1.52 g, 7.16 mmol) and benzophenone (1.32 g, 7.24 mmol) in anhydrous THF (35 mL) and anhydrous CH_2Cl_2 (50 mL) was added dropwise to the mixture. The reaction mixture was then refluxed for 24 h. After cooling to room temperature, 5% aqueous potassium carbonate (120 mL) was added to the mixture, and it was stirred for additional 2 h. Then the mixture was filtered off, and THF was removed under reduced pressure. The residue was extracted with CH_2Cl_2, and the organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was purified by silica gel column chromatography

($CHCl_3$/hexane = 1/2) to obtain **3** as a white solid (591 mg, 23%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.12-6.99 (15H, m), 6.93 (2H, d, J = 8.8 Hz), 6.63 (2H, d, J = 8.8 Hz), 3.74 (3H, s).

Synthesis of 1-hydroxy-4-(1,2,2-triphenylethynyl)benzene (4)

In a 50 mL two-necked flask, compound **3** (500 mg, 1.38 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL), and cooled to 0 °C. To the solution was added dropwise 1.0 M BBr_3 in CH_2Cl_2 (3.5 mL, 3.5 mmol), After stirring for 1 h at 0 °C, the reaction mixture was stirred for additional 16 h at room temperature. Then, distilled water (10 mL) was added dropwise to the mixture at 0 °C, and stirred for 1 h. The mixture was extracted with CH_2Cl_2, and the organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure to afford **4** as a whit solid (469 mg, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.12-6.99 (15H, m), 6.89 (2H, d, J = 8.8 Hz), 6.56 (2H, d, J = 8.8 Hz), 4.31 (1H, s).

Synthesis of 1-acryloxy-4-(1,2,2-triphenylethynyl)benzene (A1)

In a 50 mL two-necked flask, compound **4** (261 mg, 0.751 mmol) was dissolved in anhydrous CH_2Cl_2 (15 mL), and cooled to 0 °C. To the solution was added triethylamine (150 mg, 1.48

mmol), and then acryloyl chloride (230 mg, 2.54 mmol) was added dropwise, followed by stirring for 22 h at room temperature. The reaction mixture was washed with saturated aqueous sodium hydrogen carbonate and distilled water. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography ($CHCl_3$/hexane = 1/1) to afford **A1** as a white solid (240 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.14-7.01 (17H, m), 6.88 (2H, d, J = 8.6 Hz), 6.56 (1H, dd, J = 17.3, 1.2 Hz), 6.27 (1H, dd, J = 17.3, 10.4 Hz), 5.98 (1H, dd, J = 10.4, 1.2 Hz).

General procedure for preparation of network polymers

In a 10 mL snap vial, monomer (1.0 g), crosslinker (0.8 mol% of each acryloyl group to monomer) were dissolved in anhydrous DMF (1.3 eq. for monomer, to prepare 10 M monomer solution). Then the solution was purged with nitrogen gas for 30 min, and AIBN (1 mol% to monomer) was added. The reaction mixture was poured into a Teflon mold (H40×W20×D1 mm), and allowed to still stand for 24 h at 60 °C. The obtained network polymer was immersed in DMF for 24 h, and followed by drying in vacuum oven at 40 °C. The sample for measurement (H20×W5) was cut out of the obtained network polymer sheet.

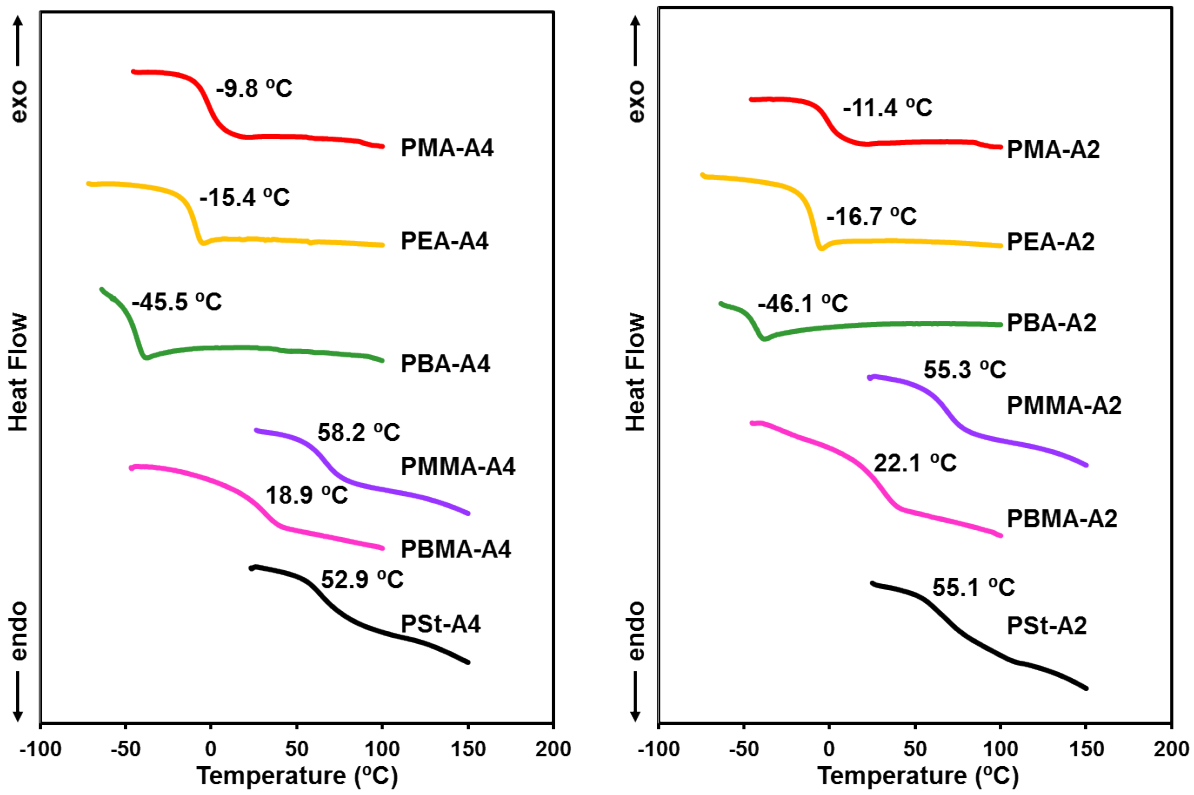


Fig.S1 DSC chart of the obtained network polymers.

Table S1. Emission behaviour of the network polymers from **A1**

	λ_{em} (nm)	QY[a]
PBA-A1	479	0.10
PBMA-A1	473	0.30
PMMA-A1	463	0.46
powder	439	0.06

[a] Absolute fluorescence quantum yield measured by using an integral sphere.

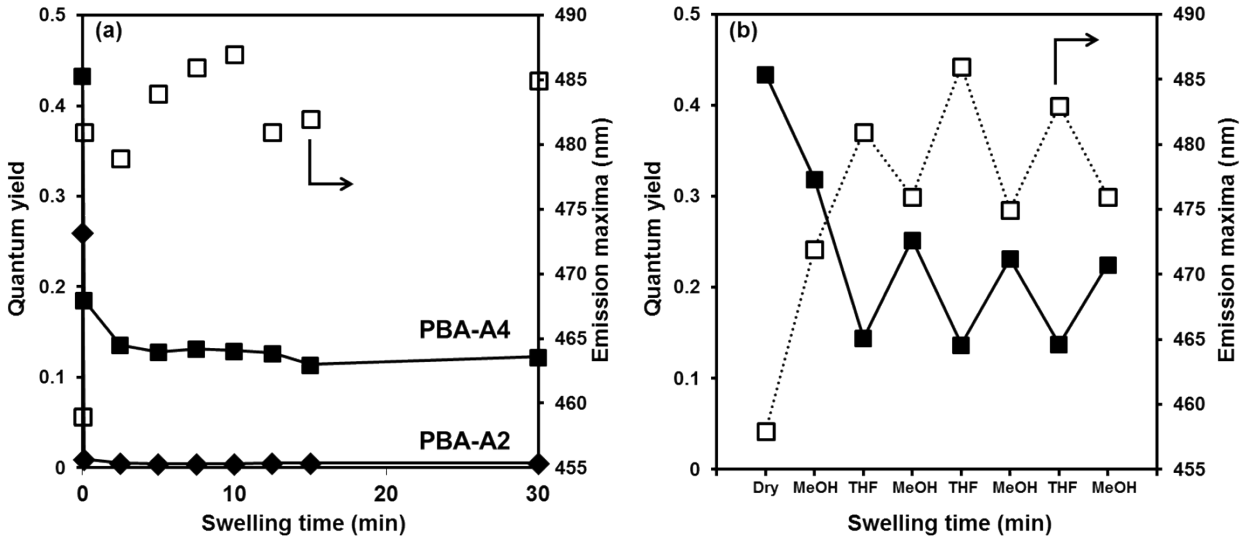


Fig. S2 (a) Time-dependent absolulte fluorescence quantum yield (QY) transition of **PBA-A4** (square) and **PBA-A2** (diamond) upon immersion in good solvent (THF). The open square represents emission maxima of **PBA-A4** at each time. (b) Absolulte fluorescence quantum yield (QY, filled square) and emission maxima (open square) of **PBA-A4** upon altanative immersion in good (THF) and poor (MeOH) solvent. Immmersion time = 1 min.

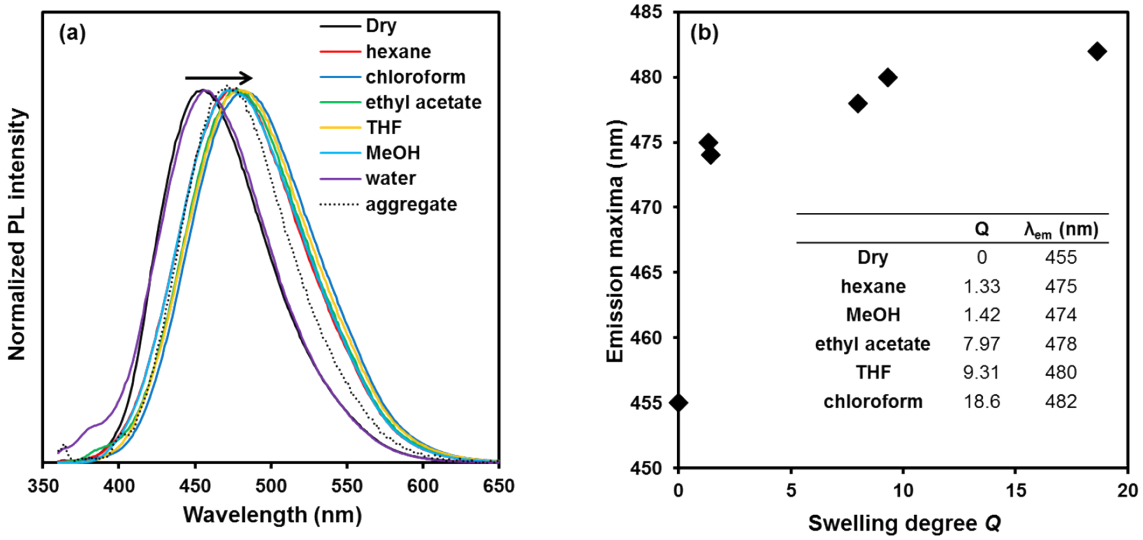


Fig. S3 (a) Fluorescence spectra of **PBA-A4** in various solvent. Excitation wavelength = 350 nm. (b) Emission maxima of **PBA-A4** in various solvent. Inset represents the relationship between swelling degree (Q) and emission maxima. The swelling degree was determined as follows; $Q = (W_{wet}-W_{dry})/W_{dry}$ (W_{wet} : weight of wetted state, W_{dry} :weight of dried state). Immmersion time = 24 h.

Reference

1. T. Noguchi, T. Shiraki, A. Dawn, Y. Tsuchiya, L. T. N. Lien, T. Yamamoto, S. Shinkai, *Chem. Commun.*, 2012, **48**, 8090.