Supporting Information to:

A High Triplet-Energy Polymers: Synthesis and Photo-Physical Properties of a π-Stacked Vinyl Polymers Having Xanthone Moiety in the Side Chain

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Contents

Experimental details

Materials

The chemicals listed as follows were used without further purification: 3-hydroxyxanthone (TCI), methacryloyl chloride (TCI), 4-dimethylaminopyridine (DMAP) (TCI), sodium hydroxide (NaOH) (Kanto Chemical), FIrpic (Sigma-Aldrich), xanthone (TCI), acetyl chloride (Kanto Chemical), pyridine (Kanto Chemical), methanol (MeOH) (Kanto Chemical), ethylbenzene (TCI), and poly(methyl methacrylate) (poly(**MMA**)) (M_n 57,400, M_w/M_n 1.39 vs. standard polystyrene, Wako Chemical). Toluene (Kanto Chemical) and chloroform (Kanto Chemical) were used after degassing. Dichloromethane (Kanto Chemical) was dried over calcium hydride and distilled before use. α,α'-Azobisisobutyronitrile (AIBN) (Wako Pure Chemical) was purified by recrystallization from MeOH. Diazomethane was prepared according to the literature.[1]

Measurements

NMR spectra were recorded on a JEOL ESC400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) and ESC600 (600 MHz for ^{1}H, 150 MHz for ^{13}C) spectrometers. Size exclusion chromatography (SEC) measurements were carried out using a chromatographic system consisting of a JASCO PU-2080 plus intelligent HPLC pump, a JASCO UV-2075 plus intelligent UV-VIS detector (254 nm), and a JASCO RI-930 intelligent RI detector equipped with TOSOH TSKgel G3000H HR and G6000H HR columns (30 × 0.72 (i.d.) cm) connected in series (eluent $CHCl_3$, flow rate 1.0 mL/min). UV-vis absorption spectra were measured at room temperature with a JASCO V-570 spectrophotometer. Photo-luminescent spectra were taken on a JASCO FP-8500 fluorescence spectrophotometer in the setting of PMT voltage: 300 V (for $CHCl_3$ solutions), and 350 V (for films), λ_{ex}: 338 nm, excitation band and fluorescence band: 5 nm, rate of scanning: 200 nm min^{-1}, and input range: 1 nm. FT-IR spectra were measured using a Thermo Fischer Scientific Nexus 870 spectrometer. Differential scanning calorimetry (DSC) analyses were performed on Rigaku Thermo plus TG8120 and DSC8230 apparatuses using Thermo plus 2 software for data analyses. Film thickness was measured using a Keyence VK-9700 Color 3D Laser Scanning Microscope (a laser confocal microscope).

Synthesis of xanthon-3-yl methacrylate (XOMA)

To a solution of 3-hydroxyxanthone (2.1 g, 10 mmol) and DMAP (0.12 g, 1.0 mmol) in CH_2Cl_2 (30 mL) was added pyridine (0.73 mL, 9.0 mmol) and methacryloyl chloride (1.5 mL, 15 mmol). The mixture was stirred for 20 h at room temperature. To the reaction mixture was added H_2O and the organic layer was separated from the aqueous layer. The aqueous layer was extracted with CH_2Cl_2 two times. The combined organic layer was washed with brine, dried over $MgSO_4$, and then filtered. The crude product obtained by concentrating the filtrate was subjected to column chromatography (SiO_2, CH_2Cl_2/hexane = 3/1) to give **XOMA** (2.4 g, 86%) as a white solid. m.p. 137–139 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.38 (d, 1H, J = 8.6 Hz), 8.35 (dd, 1H, J = 1.8, 8.2 Hz), 7.74 (ddd, 1H, J = 1.8, 7.2, 8.5 Hz), 7.50 (dd, 1H, J = 0.90, 8.5 Hz), 7.41 (ddd, 1H, J = 0.90, 7.2, 8.2 Hz), 7.36 (d, 1H, J = 1.8 Hz), 7.18 (dd, 1H, J = 1.8, 8.6 Hz), 6.42 (s, 1H), 5.85 (s, 1H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 176.3, 164.8, 156.7, 156.2, 155.7, 135.3, 134.8, 128.3, 128.1, 126.6, 124.1, 121.7, 119.5, 118.2, 117.8, 110.8, 18.3; IR (KBr) υ/cm^{-1}: 3055, 2932, 1733, 1662, 1618, 1608, 1464, 1433, 1345, 1316, 1247, 1222, 1209, 1182, 1157, 1143, 1121, 1107, 1005, 987, 958, 936, 884, 827, 802, 760, 665; LR-MS (APCI) m/z (%): 303.06 (100, $(M+Na)^+$); HR-MS (APCI): calcd. for $C_{17}H_{12}O_4$+Na: 303.0628; found: 303.0632. NMR spectra are shown in Figure S1.

Synthesis of xanthone-3-yl acetate

To a solution of 3-hydroxyxanthone (1.0 g, 4.7 mmol) and DMAP (58 mg, 0.47 mmol) in dry CH_2Cl_2 (14 mL) was added acetyl chloride (0.40 mL, 5.7 mmol) and pyridine (0.34 mL, 4.2 mmol). The mixture was stirred for 3.5 h at room temperature. To the reaction mixture was added H_2O and CH_2Cl_2, and then the organic layer was separated from the aqueous layer. The aqueous layer was extracted with CH_2Cl_2 two times). The combined organic layer was washed with H_2O and brine respectively, dried over $MgSO_4$, and then filtered. The crude product obtained by concentrating the filtrate was subjected to column chromatography (SiO_2, CH_2Cl_2) to give xanthone-3-yl acetate (1.2 g, 98%) as a white solid. All spectral data were identical with those reported in the literature;[2] m.p. 161–162 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.36 (d, 1H, *J* = 8.2 Hz), 8.34 (dd, 1H, *J* = 1.4, 7.6 Hz), 7.73 (ddd, 1H, *J* = 1.4, 8.2, 8.9 Hz), 7.49 (dd, 1H, *J* = 1.4, 8.9 Hz), 7.40 (ddd, 1H, *J* = 1.4, 7.6, 8.2 Hz), 7.36 (d, 1H, *J* = 2.1 Hz), 7.18 (dd, 1H, *J* = 2.1, 8.2 Hz), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 176.26, 168.42, 156.65, 156.15, 155.37, 134.79, 128.11, 126.62, 124.08, 121.65, 119.55, 118.07, 117.82, 110.75, 21.12; IR (KBr) υ/cm^{-1}: 3099, 3074, 1755, 1662, 1617, 1607, 1465, 1433, 1374, 1318, 1248, 1202, 1139, 1106, 1015, 983, 903, 834, 759, 694, 666; LR-MS (ESI) *m/z* (%): 277 ($[M+Na]^+$, 100), 213 (52).

Typical procedure for radical polymerization (Run 3 in Table 1)

XOMA (500 mg, 1.8 mmol) and AIBN (5.9 mg, 0.036 mmol) were placed in a flame-dried glass ampoule sealed with a three-way stopcock, which was then evacuated on a vacuum line and flushed with dry N_2 gas. Degassed $CHCl_3$ (1.2 mL) was added to dissolve the solid materials. Polymerization was carried out by heating the solution at 60 ºC in the dark. After 24 h, the reaction mixture was cooled to 0 ºC. The product was reprecipitated in a large excess of MeOH (400 mL), and the MeOH-insoluble part was collected with a centrifuge and dried under reduced pressure. MeOH-insoluble product (poly(**XOMA**)) was obtained as white powder (460 mg, 92%): ^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm: 8.27–8.05 (m), 8.05–7.78 (m), 7.50–7.28 (m), 7.20–6.82(m), 2.79–2.14 (m), 1.80–1.21 (m); ^{13}C NMR (150 MHz, $CDCl_3$) δ/ppm: 175.71, 174.94, 174.66, 174.07, 173.94, 156.39, 156.24, 155.70, 154.88, 134.91, 134.79, 128.24, 128.19, 127.92, 126.39, 124.07, 121.26, 119.74, 119.55, 117.51, 110.65, 54.67, 52.92, 46.15, 46.07, 20.77, 19.63; IR (KBr) υ/cm^{-1}: 3487, 3072, 3067, 2986, 2953, 1755, 1667, 1619, 1605, 1464, 1436, 1344, 1320, 1243, 1225, 1141, 1105, 1084, 974, 925, 888, 853, 756, 665; T_m: 170.1 ºC; T_d: 310.3 ºC; No T_g was observed in a range from –20 to 300 ºC.

Transformation of poly(XOMA) to poly(methyl methacrylate) (Poly(MMA))

Poly(**XOMA**) (50 mg) was added to a solution of NaOH in MeOH (10 mg/mL). The mixture was refluxed for 23 h. The reaction mixture was neutralized with 1.0 M aqueous HCl. A solution of diazomethane in diethyl ether was added to the mixture until the mixture became pale yellow colored. After quenching excess diazomethane by the addition of a mixture of acetic acid/MeOH (1:1 v/v), the mixture was poured into a large excess of MeOH. MeOH-insoluble part was collected with a centrifuge and dried under reduced pressure. The MeOH-insoluble product (poly(**MMA**)) was obtained as white powder (13 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 3.60 (br s, $-CO_2C\mathit{H}_3$), 1.81–1.93 (m, $-C\mathit{H}_2-$), 0.83–1.25 (m, α-$C\mathit{H}_3$) (Figure 1).

Film sample preparation

Typical procedure of film sample preparation is described for poly(**XOMA**) and FIrpic system. Poly(**XOMA**) (11.2 mg, 0.040 mmol) and FIrpic (14.1 mg, 0.020 mmol) were independently dissolved in 20 mL of $CHCl_3$. The solutions were diluted to 1.0×10^{-3} M. The polymer solution and FIrpic solution were mixed the ratios shown in Fig. 3A. A film was prepared by drop casting the solution onto a quartz glass plate (1 cm × 2 cm × 1 mm (thickness)). Film thickness data are summarized in Table S2, and photographs of the film samples are summarized in Figure S11.

DFT calculation of excited state energy

DFT calculations were performed by using the Gaussian09W Rev. C01 packages[3] in order to optimize molecular conformation and to estimate S_0, S_1, and T_1 energy levels of molecules. Molecular conformations were optimized by the B3LYP method with the 6-31G(d) basis set in the ground state (S_0) with the spin state set to singlet. The ground-state molecular coordinates were used for calculation of energies of singlet excited (S_1) and triplet excited (T_1) states. The energies of singlet excited state and triplet excited state were determined by the differences in energies between S_1 and S_0 or between T_1 and S_0.

Energy transfer efficiency

Energy transfer efficiency is defined as n (%) in the following equation which relates the luminescent quantum yield of a given sample (Y) normalized to the FIrpic concentration of the sample at <FIrpic> = 1 to that of the sample at <FIrpic> = 1 ($Y_{<\mathrm{FIrpic}>=1}$):

$$Y = Y_{<\mathrm{FIrpic}>=1} \times [\mathrm{Abs}_{\mathrm{FIrpic}}/\mathrm{Abs}_{\mathrm{sum}} + (n/100) \times (\mathrm{Abs}_{\mathrm{polymer}}/\mathrm{Abs}_{\mathrm{sum}})]$$

where $\mathrm{Abs}_{\mathrm{sum}}$ is the total absorbance at the wavelength of excitation of the sample, and $\mathrm{Abs}_{\mathrm{FIrpic}}$ and $\mathrm{Abs}_{\mathrm{polymer}}$ are contributions of FIrpic and polymer to the total absorbance. This equation is transformed to:

$$n = 100 \times (\mathrm{Abs}_{\mathrm{sum}}/\mathrm{Abs}_{\mathrm{polymer}}) \times [Y - Y_{<\mathrm{FIrpic}>=1} \times (\mathrm{Abs}_{\mathrm{FIrpic}}/\mathrm{Abs}_{\mathrm{sum}})]/Y_{<\mathrm{FIrpic}>=1}$$

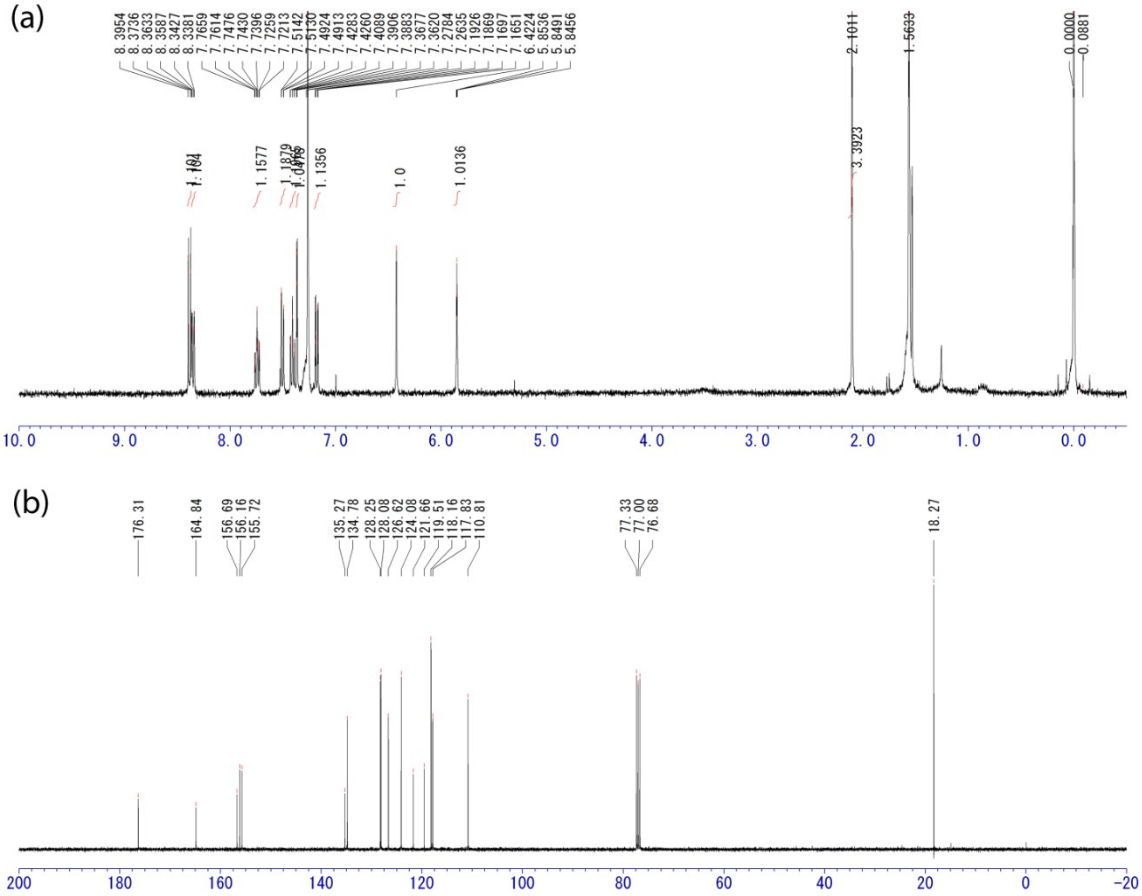


Figure S1. 400-MHz ^{1}H NMR (a) and 100-MHz ^{13}C NMR (b) spectra of **XOMA** ($CDCl_3$, 23°C).

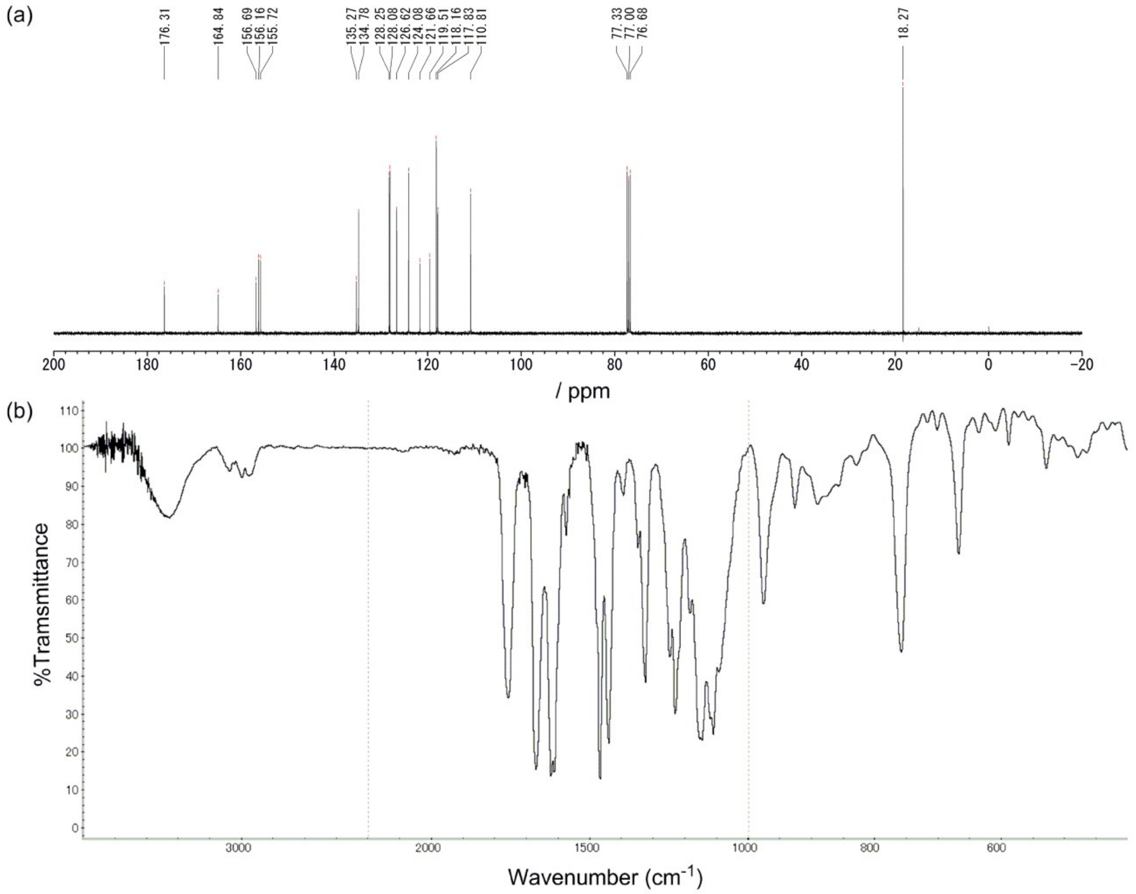


Figure S2. 150-MHz ^{13}C NMR spectrum ($CDCl_3$) (a) and FT-IR spectrum (KBr) (b) of poly(**XOMA**) (run 3 in Table 1).

Table S1. Radical copolymerization of **XOMA** and **MMA**.[a]

([**XOMA**]$_o$/[**MMA**]$_o$) in feed	Conv. of **XOMA** [b] (%)	Conv. of **MMA** [b] (%)	MeOH-insoluble polymer			
			Yield (%)	M_n[c]	M_w/M_n[c]	[**XOMA**]/[**MMA**][d] in polymer
1/1	97	86	80	8440	7.86	0.50/0.50

[a]**XOMA** = 200 mg (0.71 mmol), **MMA** = 76 μL (0.71 mmol), [M]o/[I]o = 50. [b]Determined by ^{1}H NMR ($CDCl_3$) of crude product. [c]Estimated by SEC on the basis of polystyrene standards (eluent: $CHCl_3$). [d]Estimated by ^{1}H NMR ($CDCl_3$) of purified polymer.

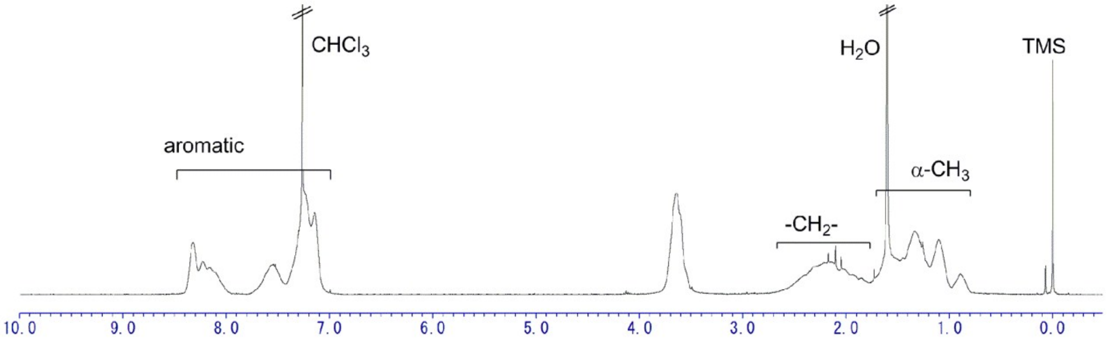


Figure S3. 400-MHz ^1H NMR spectra of poly(**XOMA**-co-**MMA**) ($CDCl_3$, 23 °C).

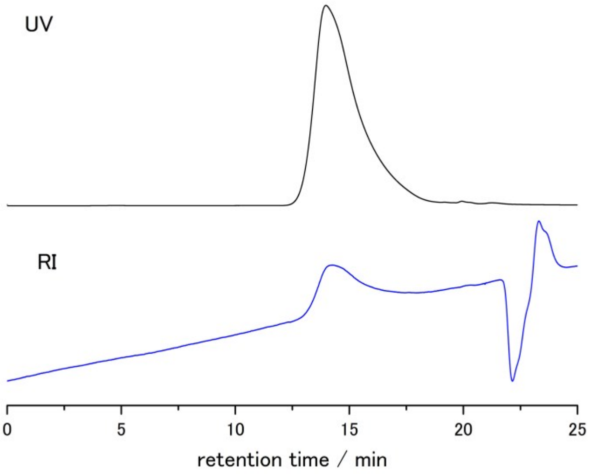


Figure S4. SEC curves of poly(**XOMA**-co-**MMA**) obtained by UV (254 nm) (top) and RI (bottom) detectors.

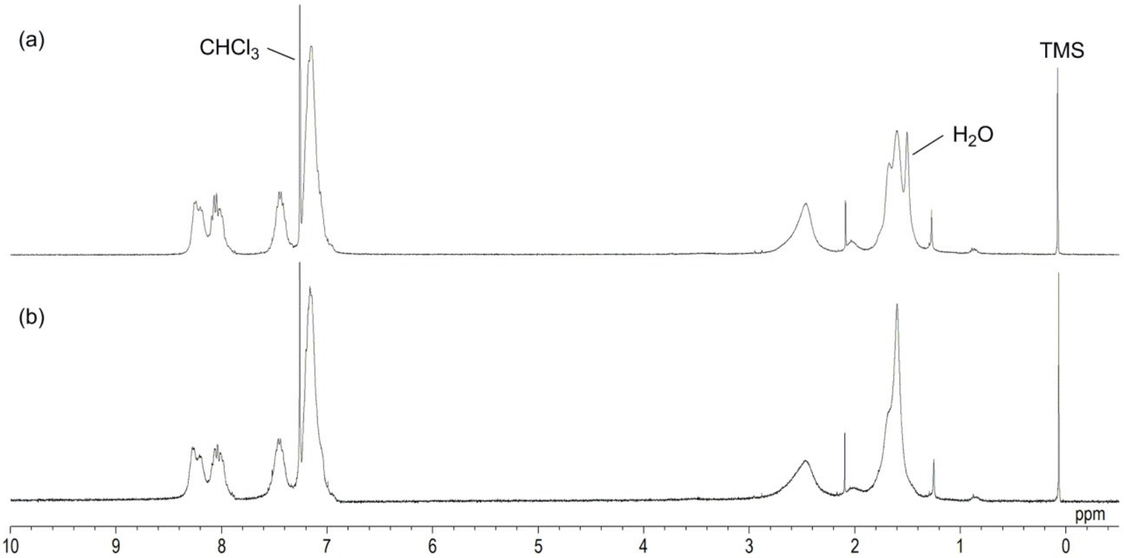


Figure S5. 400-MHz ^1H NMR spectra of poly(**XOMA**) (run 3 in Table 1) measured at 55 ºC (a) and 25 ºC (b) ($CDCl_3$).

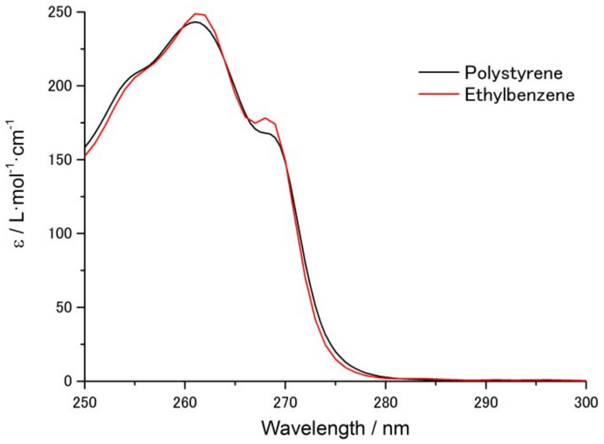


Figure S6. UV spectra of polystyrene and ethylbenzene: control data to support π-stacked structures of poly(**XOMA**) (CHCl$_3$, 23^{o}C, conc. 1 x 10^{-5}M, 1-mm cell).

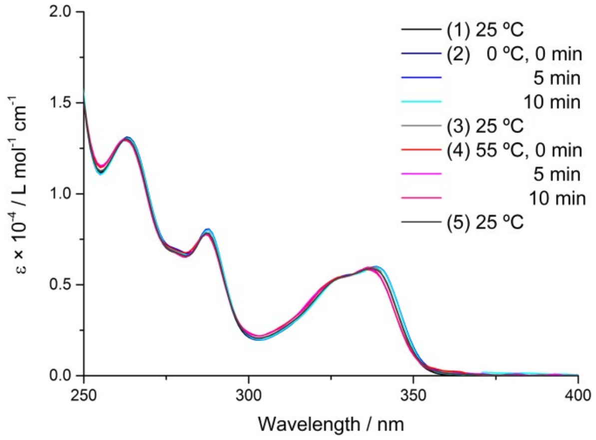


Figure S7. UV spectra of poly(**XOMA**) (run 3 in Table 1) in CHCl$_3$ measured at different temperatures at [polymer (unit residue)] = 1.0×10^{-5} M in a 1-cm quartz cell. Temperature was changed in the following order: (1) 25^{o}C, (2) 0 ^{o}C, (3) 25 ^{o}C, (4) 55 ^{o}C, and (5) 25 ^{o}C. Concentration of the sample solution was corrected considering dependence of density of CHCl$_3$ on temperature.

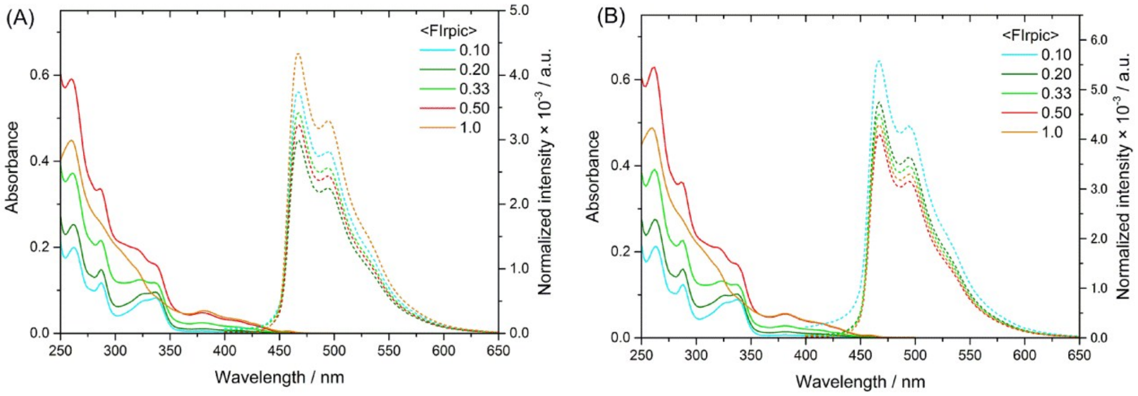


Figure S8. Absorbance and emission spectra of $CHCl_3$ solutions containing poly(**XOMA**-co-**MMA**) and FIrpic (A), and **XA** and FIrpic (B). The absorbance and emission spectra were taken in a 1-cm quartz cell at 23 °C at a constant [polymer (per unit residue) or **XA**] of 1.0×10^{-5} M and various [FIrpic] in the range of $0.11 \times 10^{-5} \sim 1.0 \times 10^{-5}$ M.

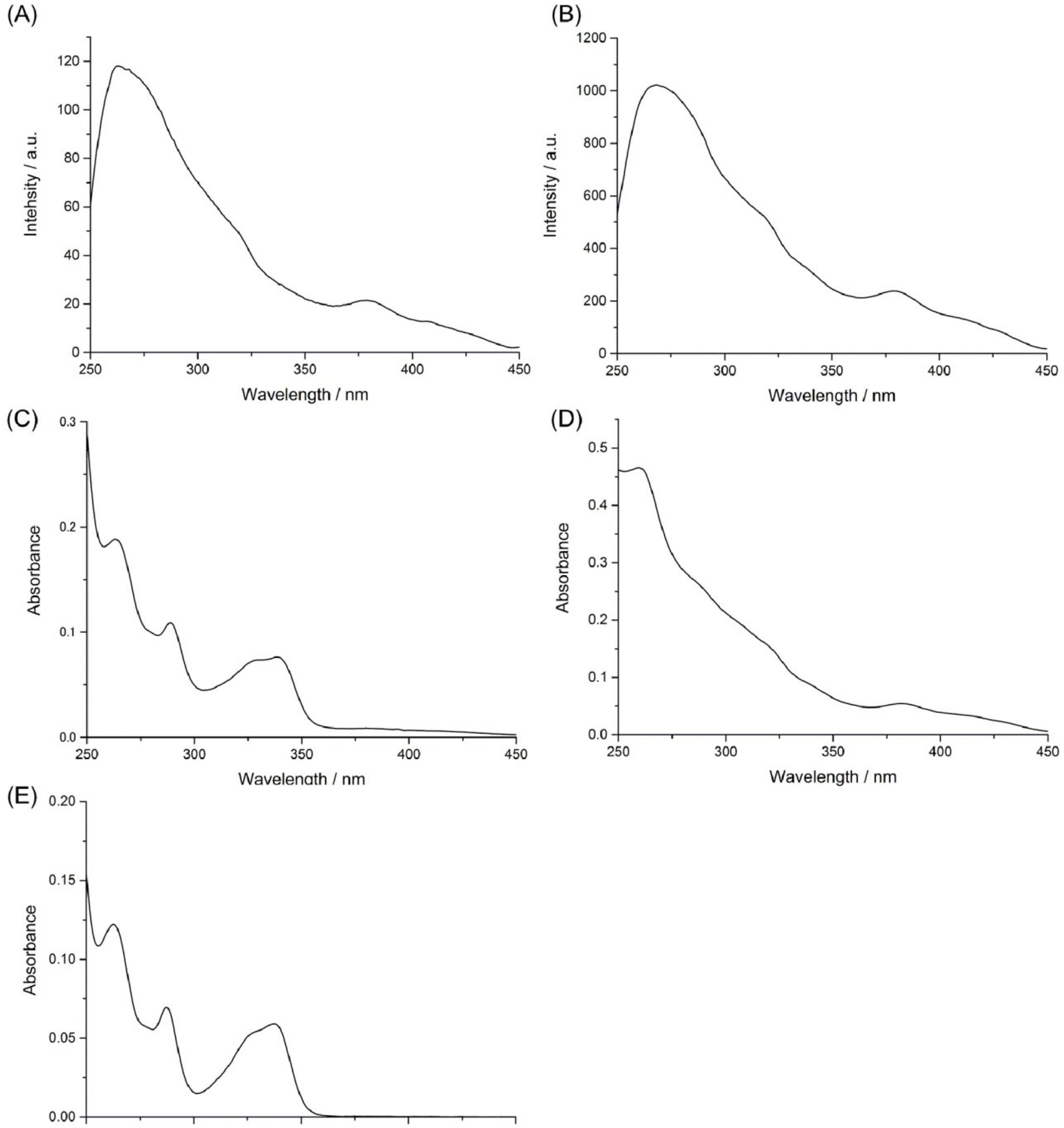


Figure S9. Excitation spectra of a poly(**XOMA**)-FIrpic solution (<FIrpic> = 0.10) (A),[a] a pure FIrpic solution (B),[b] and absorbance spectra of poly(**XOMA**)-FIrpic solution (<FIrpic> = 0.10) (C),[a] a pure FIrpic solution (D),[b] and a pure poly(**XOMA**) solution (E).[c]

[a] [Poly(**XOMA**) (per unit residue)] = 1.0×10^{-5} M, [FIrpic] = 0.11×10^{-5} M, 23 ºC.
[b] [FIrpic] = 1.0×10^{-5} M, 23 ºC. [c] [Poly(**XOMA**) (per unit residue)] = 1.0×10^{-5} M, 23 ºC.

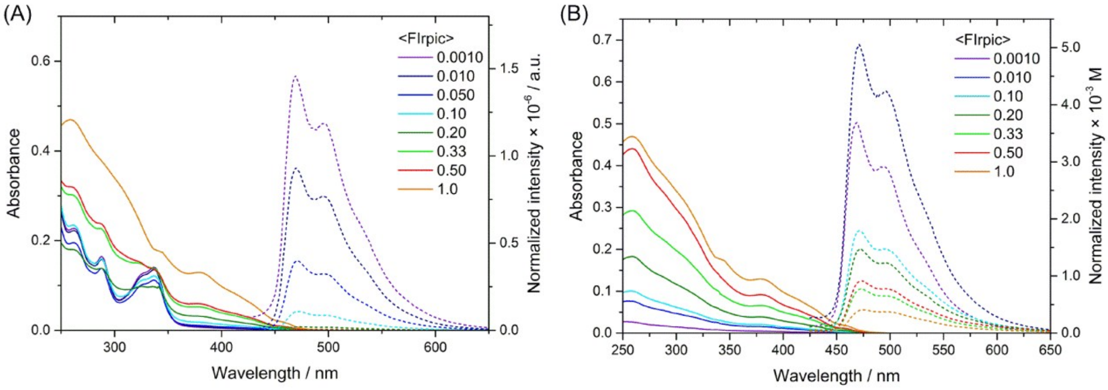


Figure S10. Absorbance and emission spectra of cast films containing poly(**XOMA**-co-**MMA**) and FIrpic (A), and poly(**MMA**) and FIrpic (B).

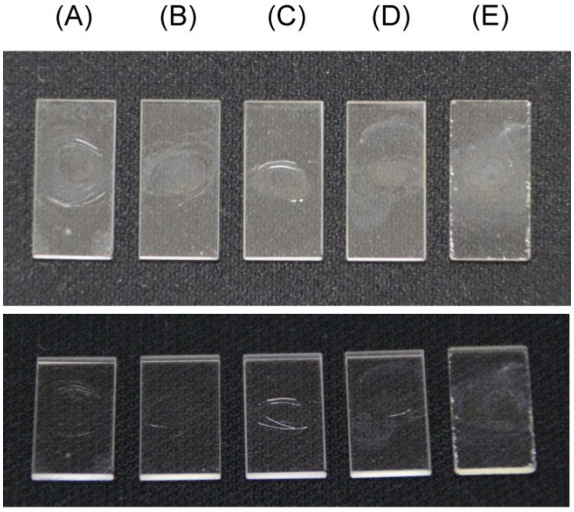


Figure S11. Photographs of cast films. Poly(**XOMA**) (A), poly(**XOMA**)–FIrpic (<FIrpic> = 0.50) (B), poly(**XOMA**-co-**MMA**) (C), poly(**XOMA**-co-**MMA**)–FIrpic (<FIrpic> = 0.50) (D), and pure FIrpic (E).

Table S2. Thicknesses of film samples

Polymer	<FIrpic>	Thickness[a] / μm
Poly(**XOMA**)	0	0.13
	0.010	0.12
	0.050	0.19
	0.10	0.15
	0.20	0.13
	0.33	0.15
	0.50	0.14
Poly(**MMA**)	0	0.12
	0.010	0.12
	0.050	0.16
	0.10	0.15
	0.20	0.15
	0.33	0.16
	0.50	0.16
FIrpic	1.0	0.14

[a] Measured using a laser confocal microscope.

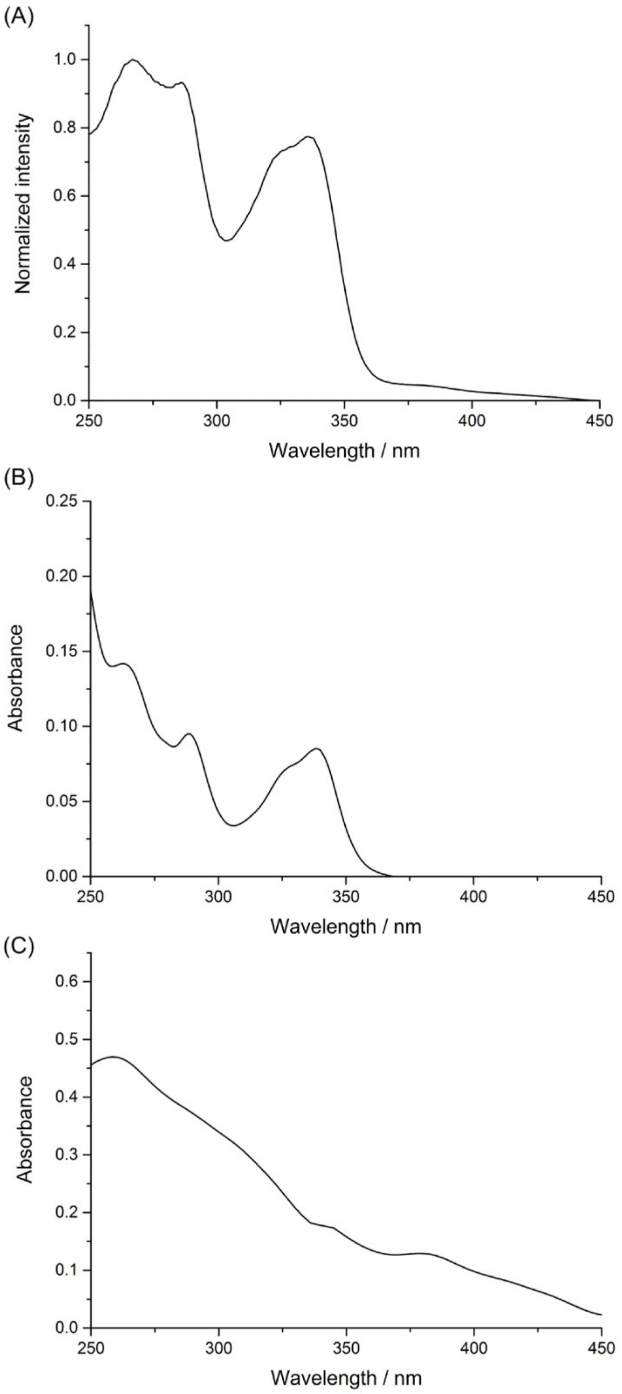
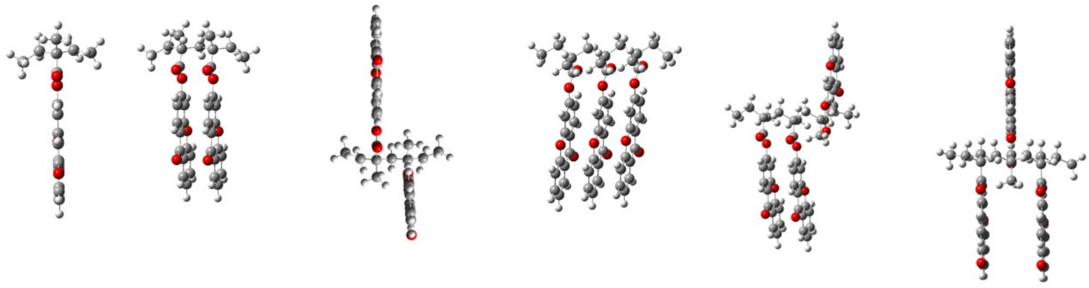
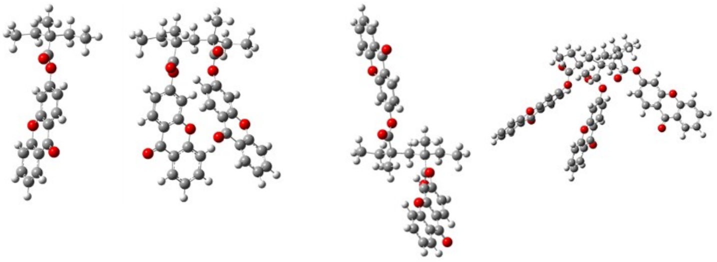


Figure S12. Excitation spectrum of a poly(**XOMA**)-FIrpic film (<FIrpic> = 0.010) (A), and absorbance spectra of poly(**XOMA**) film (B) and pure FIrpic film (C).

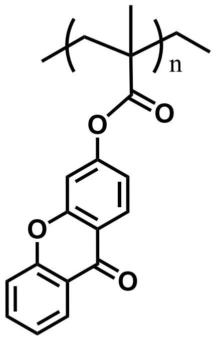
A. Unoptimized structures


unimer m dimer r dimer mm trimer mr trimer rr trimer

B. Optimized structures


unimer m dimer r dimer mm trimer mr trimer rr trimer

C. Chemical structure



unimer: n = 1
dimer: n = 2
trimer: n = 3

Figure S13. Structures of unoptimized (A) and optimized (B) unimer, meso (m) dimer, raceme (r) dimer, mm trimer, mr trimer, and rr trimer and chemical structure of the oligomers (C). Optimization was performed by DFT using the B3LYP method with the 6-31G(d) basis set.

Table S3. S_1 and T_1 energies of oligomers[a]

Oligomer	Optimization	S_1 energy $\Delta(S_1–S_0)$ / eV	T_1 energy $\Delta(T_1–S_0)$ / eV
unimer	No	3.61	3.15
m dimer	No	1.03	1.23
r dimer	No	3.59	3.40
mm trimer	No	1.22	1.48
mr trimer	No	2.18	2.36
rr trimer	No	3.59	3.13
unimer	Yes	3.62	3.17
m dimer	Yes	3.61	3.16
r dimer	Yes	3.62	3.43
mm trimer	Yes	3.61	3.23
mr trimer	Yes	3.52	3.27
rr trimer	Yes	3.61	3.24

[a] By DFT calculations using the B3LYP method with the 6-31G(d) basis set

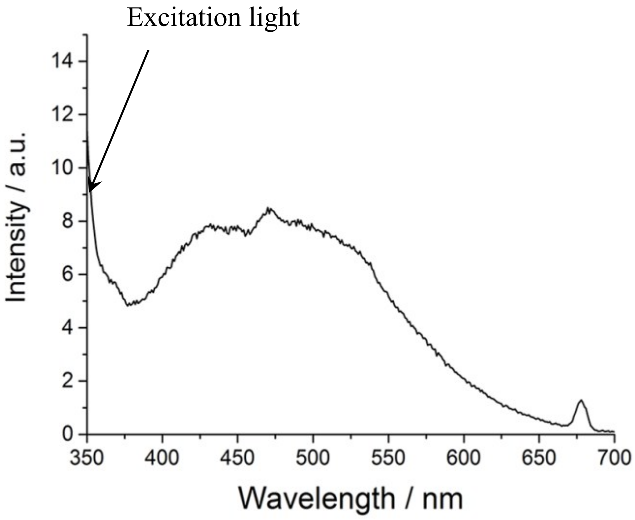


Figure S14. Emission spectrum of the pure poly(XOMA) film at <FIrpic> = 0 obtained at excitation at 338 nm at room temperature in the air.

References for Supporting Information

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[3]. Gaussian 09, Revision **C.01**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O.

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