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

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Poly(xanthon-3-yl methacrylate) (poly(XOMA)) and poly(xanthon-3-yl methacrylate-co-methyl methacrylate) (poly(XOMA-co-MMA)) having a π -stacked conformation were synthesized as host material candidates for phosphorescence-based light emitting diodes. Poly(XOMA) harvested photo excitation energy for blue phosphorescent emission of iridium bis[(4,6-difluorophenyl)pyridinato- N,C^2]picolinate (FIrpic) in a CHCl_3 solution and in film.

Phosphorescence-emitting diodes (LEDs) have been recognized to be more important than fluorescent ones^{1–6} because the internal fluorescence quantum yield (Φ) is at maximum around 25%⁷ and the quantum yield of phosphorescent emitting materials can reach almost 100%. In constructing a phosphorescent OLED device, development of a polymeric host material dispersing emitting compounds is indispensable. Energy transfer may occur from a triplet-excited host to an emitter to give a triplet excited state. It is also possible that a singlet-excited host excites a triplet emitter to lead to a singlet excited state and a triplet-excited emitter is formed through intersystem crossing. In either case, a good host material has to have a higher lowest triplet (T_1) energy level compared with that of a phosphorescent emitter and efficient singlet or triplet energy transport (migration) ability. Existing host materials include carbazole derivative,^{8–14} triphenylamine derivatives,¹⁵ triazine derivatives,^{16,17} and polyfluorenes.^{18,19} However, xanthone-based polymers have not been explored as a triplet host while xanthone has a T_1 energy (3.21 eV)^{20,21} which is higher than that of blue-phosphorescent iridium bis[(4,6-difluorophenyl)pyridinato- N,C^2]picolinate (FIrpic: T_1 2.65 eV).⁹ Herein, we report the synthesis and properties of poly(xanthon-3-yl methacrylate) (poly(XOMA)) and poly(xanthon-3-yl methacrylate-co-methyl methacrylate) (poly(XOMA-co-MMA)) as well as xanthon-3-yl acetate (XA) as a model compound of monomeric unit (Chart 1). Polymers having xanthone moiety in the side chain have never been

reported so far to the best of our knowledge. Even polymers having xanthone moiety in the main chain are limited to rather early examples such as a polymer made by Friedel-Crafts polymerization^{22a,b} and a polyamide.^{22c}

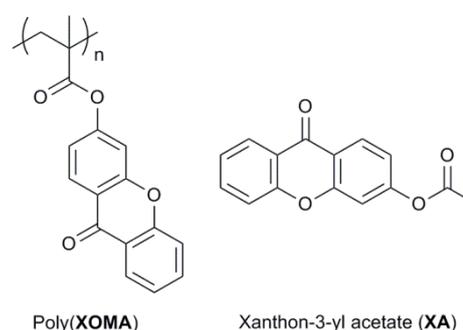


Chart 1. Structures of poly(XOMA) and XA as a unit model.

Results and discussion

The monomer, XOMA, was synthesized via condensation of 3-hydroxyxanthone with methacryloyl chloride. Radical polymerization of XOMA was carried out using α,α' -azobisisobutyronitrile (AIBN) in CHCl_3 at different $[\text{M}]_0/[\text{I}]_0$ ratios in the dark in order to avoid xanthone-sensitized radical reactions (Table 1). The polymerizations resulted in almost quantitative conversions, and molar mass of the product can be moderately changed by altering $[\text{M}]_0/[\text{I}]_0$ ratio. The obtained polymers were soluble in solvents including CHCl_3 and tetrahydrofuran. Poly(XOMA) (run 3 in Table 1) did not show a clear T_g and started to decompose at T_{decomp} of 310.3 °C in thermal analyses. Radical copolymerization of XOMA with methyl methacrylate (MMA) was also carried out at a feed monomer ratio of 1/1 at $[\text{MMA}]_0 = [\text{XOMA}]_0 = 0.75$ M, $[\text{AIBN}]_0 = 0.030$ M, at 60 °C for 24 h to afford a copolymer of M_n 8440 and M_w/M_n 7.86 (SEC vs

Table 1. Radical polymerization of **XOMA** in CHCl_3 .^a

Run	$[\text{M}]_0/[\text{I}]_0$	Conv. ^b (%)	MeOH-insoluble polymer		
			Yield (%)	M_n^c	M_w/M_n^c
1	10	>99	97	8,500	5.52
2	25	>99	92	10,800	6.03
3 ^d	50	>99	92	12,100	8.32
4	100	>99	92	22,700	5.03

^a**XOMA** = 100 mg (0.36 mmol) (runs 1,2, and 4), 500 mg (1.8 mmol) (run 3). ^bDetermined by ^1H NMR (CDCl_3). ^cEstimated by SEC on the basis of polystyrene standards (eluent: CHCl_3). ^dTriad tacticity was mm/mr/rr = 8/40/52 as determined by ^1H NMR of **PMMA** converted from the MeOH-insoluble part of poly(**XOMA**).

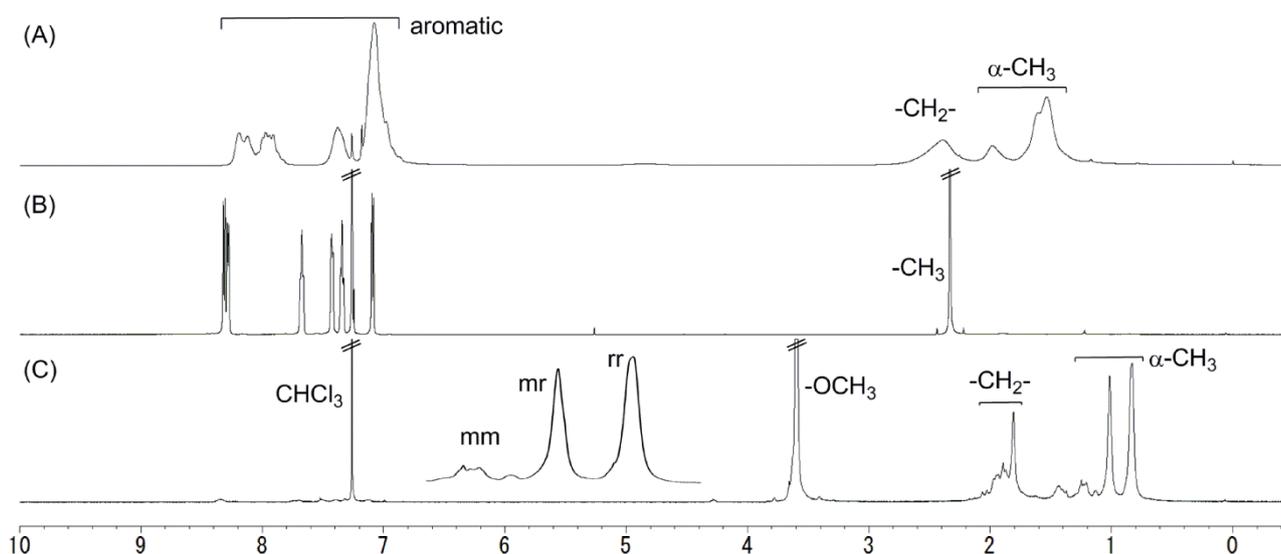


Fig. 1. ^1H NMR spectra of poly(**XOMA**) (run 3 in Table 1) (A), **XA** (a unit model for poly(**XOMA**)) (B), and poly(**MMA**) converted from poly(**XOMA**) (run 3 in Table 1) (C). [400 MHz, CDCl_3 , 23 °C]

standard polystyrene) and a unit ratio, $[\text{MMA}]/[\text{XOMA}]$ in polymer of 0.50/0.50 was obtained. In SEC analyses using RI and UV (wavelength: 254 nm) detectors, the chromatograms obtained by the two detectors had very similar shapes (Fig. S4 in ESI). These results indicate that two monomeric units are randomly distributed regardless of molar mass. The polymer is most probably a random copolymer.

Fig. 1 shows the ^1H NMR spectrum of poly(**XOMA**) (run 3 in Table 1) along with those of **XA** as a model compound of monomeric unit and poly(**MMA**) derived from poly(**XOMA**). The spectrum of the poly(**XOMA**) indicated signals that are consistent with the polymer structure which was also supported by FT-IR and ^{13}C NMR spectra (Fig. S2 in ESI).

Tacticity of poly(**XOMA**) was assessed by ^1H NMR spectra of poly(**MMA**) derived from the original polymer (Fig. 1C). Poly(**XOMA**) was converted to poly(**MMA**) by hydrolysis in MeOH containing HCl followed by methylation using CH_2N_2 . The ^1H NMR spectrum of poly(**MMA**) indicated three separate signals of α -methyl group based on mm, mr, and rr triads. Poly(**XOMA**) obtained in this work is rich in syndiotacticity similarly to other polymethacrylates synthesized by free radical polymerization.²³ In the ^1H NMR spectrum shown in Fig. 1A, the aromatic proton signals are slightly up-field shifted with respect to the corresponding signals of **XA** (Fig. 1B), which suggests π -stacking of the side-chain xanthone groups. Up-field shifts have been reported for

poly(dibenzofulvene) and its derivatives having a regulated π -stacked conformation.²⁴⁻²⁶ Further, no major differences were confirmed between ^1H NMR spectra taken at room temperature and

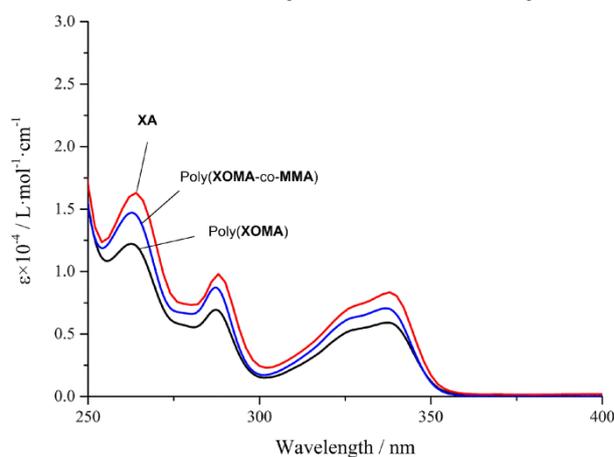


Fig. 2. UV-vis spectra of **XOMA** polymers and a unit model in CHCl_3 : poly(**XOMA**) (run 3 in Table 1) (a), poly(**XOMA-co-MMA**) (b), and **XA** (c). [conc. = 1.0×10^{-5} M, 23 °C]

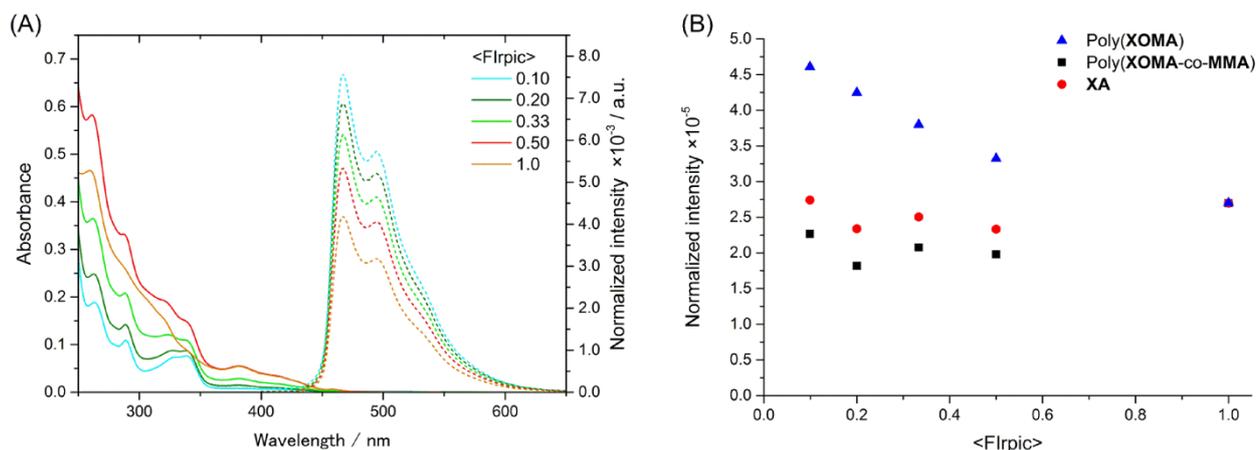


Fig. 3. Absorbance and emission spectra of CHCl_3 solution containing poly(XOMA) (run 3 in Table 1) and Flrpic (A), and a plot of normalized emission intensity against mole fraction of Flrpic for poly(XOMA) system, poly(XOMA-co-MMA) system, and control system with XA (B). The absorbance and emission spectra were taken in a 1-cm quartz cell at 23 °C at a constant [polymer (per unit residue)] of 1.0×10^{-5} M and various [Flrpic] in the range of $0.11 \times 10^{-5} \sim 1.0 \times 10^{-5}$ M for the data at $\langle \text{Flrpic} \rangle = 0.1 \sim 0.5$. The spectrum at $\langle \text{Flrpic} \rangle = 1$ corresponds to a pure Flrpic solution at $[\text{Flrpic}] = 1.0 \times 10^{-5}$ M. The absorbance and emission spectra of the poly(XOMA-co-MMA) system and the control system are in ESI (Fig. S8 in ESI).

at 55 °C in CDCl_3 ; the proposed π -stacking seems to be maintained even at an elevated temperature (Fig. S5 in ESI).

Fig. 2 shows UV-vis spectra of poly(XOMA) (run 3 in Table 1), poly(XOMA-co-MMA), and XA as a unit model. The poly(XOMA) indicated clear hypochromic effects with respect to XA, supporting that the side-chain groups are π -stacked. A connection between hypochromism and a π -stacked conformation has been established for DNAs²⁷ and poly(dibenzofulvene) and its derivatives.²⁴⁻²⁶ If a polymer has a completely random conformation, hypochromic effects are not observed, which was confirmed in this work using polystyrene and ethylbenzene as a unit model (Fig. S6 in ESI). Also, the stacking was found stable again at an elevated temperature through UV spectral measurements at various temperatures (Fig. S7 in ESI). Further, poly(XOMA-co-MMA) showed weaker hypochromism compared with the poly(XOMA); the copolymer may have a less ordered π -stacked conformation. As the chromophores in the copolymer are rather randomly distributed, the chance of aligning two xanthone groups adjacent to each other should be less than that in the homopolymer.

The extent of overlapping of π -electronic systems of poly(XOMA) and poly(XOMA-co-MMA) showing no red shifts in the UV spectra may be smaller compared with that of poly(dibenzofulvene) showing remarkable red shifts.²⁴⁻²⁶ Otherwise, spatial arrangements of stacked chromophores may be different in poly(XOMA) or poly(XOMA-co-MMA) and in poly(dibenzofulvene). π -Stacked chromophores in DNA double helices shows clear hypochromicity and no clear red shifts.²⁸

T_1 energy transfer from poly(XOMA), poly(XOMA-co-MMA), and XA to Flrpic was examined in a CHCl_3 solution at different concentrations where the concentration of polymer or XA was constant ($[\text{polymer or XA}] = 1.0 \times 10^{-5}$ M) and the concentration of Flrpic varied in the range of $[\text{Flrpic}] = 0.11 \times 10^{-5} \sim 1.0 \times 10^{-5}$ M. Fig. 3A shows the absorbance and emission spectra of the solutions containing poly(XOMA) (run 3 in Table 1) and Flrpic. The spectra for the systems with poly(XOMA-co-MMA) and XA are found in ESI (Fig. S8 in ESI). The emission spectra were recorded on excitation at 338 nm. The absorption spectral shape varied depending on the ratio of the polymer to Flrpic but emission spectral shape was unchanged and arose from Flrpic. The polymer alone

hardly emitted at room temperature, which is consistent with the fact that xanthone has a high probability of intersystem crossing leading to a triplet state in excited states and emits clear phosphorescence only at low temperature.^{21,29}

Fig. 3B indicates a plot of normalized emission intensity against the mole fraction of Flrpic which is defined as $\langle \text{Flrpic} \rangle = [\text{Flrpic}] / ([\text{Flrpic}] + [\text{polymer (unit residue) or XA}])$. Since both xanthone moiety and Flrpic absorb at 338 nm and emission arises only from Flrpic, the emission spectral intensity was normalized to the contribution of Flrpic to absorbance at 338 nm which was calculated by multiplying absorbance by $[\text{Flrpic}] \times \epsilon_{\text{Flrpic}}(338 \text{ nm}) / ([\text{Flrpic}] \times \epsilon_{\text{Flrpic}}(338 \text{ nm}) + [\text{polymer (unit residue) or XA}] \times (\epsilon_{\text{polymer (unit residue)}}(338 \text{ nm}) \text{ or } \epsilon_{\text{XA}}(338 \text{ nm})))$ where $\epsilon_{\text{Flrpic}}(338 \text{ nm})$, $\epsilon_{\text{polymer}}(338 \text{ nm})$, and $\epsilon_{\text{XA}}(338 \text{ nm})$ are molar absorptivities of Flrpic ($8380 \text{ L mol}^{-1} \text{ cm}^{-1}$), polymers (poly(XOMA) $5900 \text{ L mol}^{-1} \text{ cm}^{-1}$; poly(XOMA-co-MMA) $7020 \text{ L mol}^{-1} \text{ cm}^{-1}$ (based on XOMA unit residue)), and XA ($7750 \text{ L mol}^{-1} \text{ cm}^{-1}$), respectively, at 338 nm in CHCl_3 .

For the system with XA, normalized emission intensity of Flrpic is almost unchanged regardless of $\langle \text{Flrpic} \rangle$. In contrast, for the system with poly(XOMA), normalized emission intensity of Flrpic is slightly greater than that of the pure Flrpic solution at $\langle \text{Flrpic} \rangle = 1$. These results indicate that poly(XOMA) is excited and transfers triplet excited energy Flrpic (triplet energy harvesting) to but the degree of harvesting is rather small. The harvesting effect seems greater at a lower $\langle \text{Flrpic} \rangle$ which corresponds to a higher concentration of poly(XOMA). At a lower $\langle \text{Flrpic} \rangle$, i.e., at a higher concentration of the polymer where interactions among polymer chains and those between a chain and Flrpic should be more frequent, T_1 energy transferred through the Dexter mechanism³⁰ requiring collision of between donor and acceptor species would be facilitated. Although T_1 energy of XA was estimated to be 3.43 eV by DFT calculations at the B3LYP method using 6-31G(d) basis set and is higher enough to be a sensitizer, it did not show harvesting effects. Further, poly(XOMA-co-MMA) did not harvest triplet energy either. These results suggest that π -stacked polymer structure^{24,31} where side-chain xanthone moieties are closely interacting with each other is important in attaining triplet energy harvesting.

The shape of the excitation spectrum of the poly(XOMA) solution at $\langle \text{Flrpic} \rangle = 0.10$ was more similar to the absorption spectrum of a

pure Flrpic solution at $[\text{Flrpic}] = 1.0 \times 10^{-5} \text{ M}$ rather than to that of a pure polymer solution at $[\text{poly}(\text{XOMA}) \text{ (per unit residue)}] = 1.0 \times 10^{-5} \text{ M}$ (Fig. S9 in ESI). This observation suggests that the observed emission from Flrpic arises mainly from directly excited Flrpic, which is consistent with the conclusion that the extent of the proposed harvesting effect by poly(XOMA) is rather small in solution.

The luminescence quantum yields of the pure Flrpic solution at $\langle \text{Flrpic} \rangle = 1$ ($[\text{Flrpic}] = 1.0 \times 10^{-5} \text{ M}$) in CHCl_3 was estimated to be 45 % on excitation at 338 nm on the basis of a reported quantum yield in CH_2Cl_2 (62%, excitation at 407 nm)³² considering the differences in excitation wavelength and reflective index of the two

solvents.³³ In the same manner, the quantum yield of the solution containing poly(XOMA) and Flrpic at $\langle \text{Flrpic} \rangle = 0.1$ ($[\text{Flrpic}] = 1.0 \times 10^{-6} \text{ M}$) was estimated to be 8 % after normalization to the concentration of Flrpic at $\langle \text{Flrpic} \rangle = 1$ ($[\text{Flrpic}] = 1.00 \times 10^{-5} \text{ M}$). Based on these quantum yields, the energy transfer efficiency was determined to be 11 % at $\langle \text{Flrpic} \rangle = 0.1$ (See ESI for the definition of the energy transfer efficiency.). This means that 11% of photon energy absorbed by poly(XOMA) was transferred to Flrpic.

T_1 energy transfer from poly(XOMA) and poly(XOMA-co-MMA) to Flrpic was further investigated in the solid state using film samples. Control experiments were performed using poly(MMA)

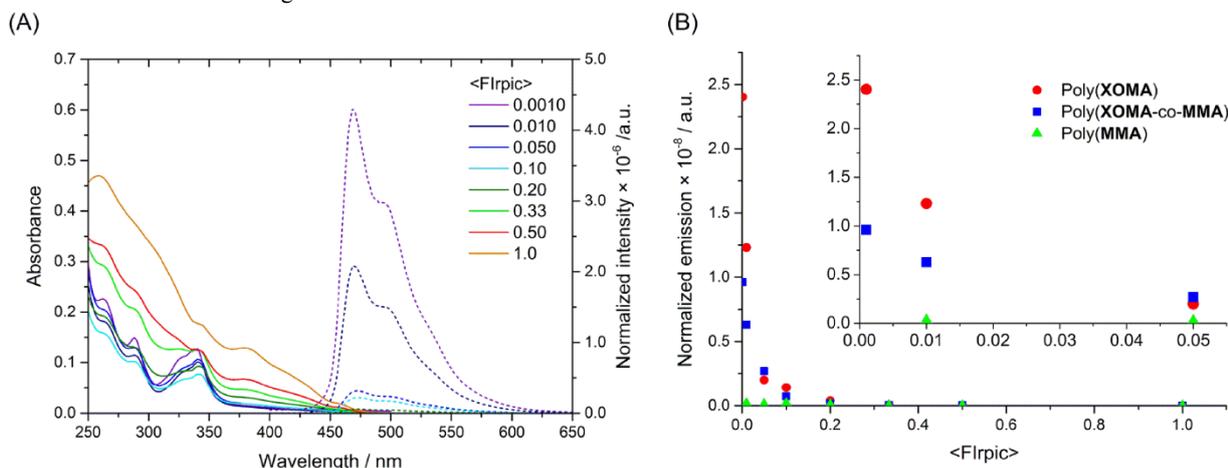


Fig. 4. Absorbance and emission spectra of cast films made from poly(XOMA) (run 3 in Table 1) and Flrpic (A), and a plot of normalized emission intensity against mole fraction of Flrpic for the poly(XOMA) film, poly(XOMA-co-MMA) film containing Flrpic and control film made of poly(MMA) containing Flrpic (B). The absorbance and emission spectra of the poly(XOMA-co-MMA) films and the poly(MMA) films and the photographs and thickness data of the film samples are in ESI (Fig. S11 and Table S2 in ESI).

which would not harvest triplet energy. Polymer films containing Flrpic at different mole fractions were fabricated on a quartz plate by a drop casting method, and their absorbance spectra and emission spectra on excitation at 338 nm were measured. Emission intensity was normalized to absorbance of Flrpic at 338 nm where light is absorbed both by polymer and Flrpic. Flrpic's contribution to absorbance at 338 nm was estimated by multiplying observed absorbance by $\langle \text{Flrpic} \rangle \times \epsilon_{\text{Flrpic}}(338 \text{ nm}) / (\langle \text{Flrpic} \rangle \times \epsilon_{\text{Flrpic}}(338 \text{ nm}) + \langle \text{polymer (unit residue)} \rangle \times \epsilon_{\text{polymer (unit residue)}}$ where $\langle \text{Flrpic} \rangle$ and $\langle \text{polymer (unit residue)} \rangle$ are mole fractions of Flrpic and polymer in a film, respectively, and ϵ values are those in CHCl_3 solution.

The absorbance and emission spectra for the poly(XOMA) films are shown in Fig. 4A. The spectra for the other films are found in ESI (Fig. S10 in ESI). The spectral patterns of the films were similar to those in solution, suggesting that the films are rather homogeneous and that photo physical properties are not significantly affected by diffraction and reflection effects. This is supported by the fact that the films were smooth and transparent (Fig. S11 in ESI). Further, thicknesses of the films were ca. 0.12 ~ 0.19 μm where diffraction and reflection should not occur on irradiation at 338 nm and emission at around 450~600 nm (Table S2 in ESI).

Normalized intensities of the film samples were plotted against $\langle \text{Flrpic} \rangle$ (Fig. 4B). The data point at $\langle \text{Flrpic} \rangle = 1$ corresponds to a film sample fabricated using pure Flrpic. In the low $\langle \text{Flrpic} \rangle$ range (<0.01), films of poly(XOMA) emit light whose intensity is as much as 1000 times greater than that emitted by a pure Flrpic film sample on direct excitation or from the poly(MMA) films containing Flrpic, strongly indicating that poly(XOMA) very efficiently harvests triplet energy. The fact that emission intensity is greater at a lower $\langle \text{Flrpic} \rangle$ implies that direct interaction between Flrpic species

hampers effective emission and that complete dispersion of Flrpic in a film is important in devising an efficient phosphorescent emitting material. In addition, poly(XOMA-co-MMA) also showed harvesting effects which were weaker than those of poly(XOMA), indicating that an ordered π -stacked structure of the poly(XOMA) plays an important role in energy harvesting in the solid state as well as in solution. Triplet energy migration between xanthone moieties may be remarkably enhanced by the stacked alignment of π -electron systems.

The shape of the excitation spectrum of the poly(XOMA) film at $\langle \text{Flrpic} \rangle = 0.010$ was more similar to the absorption spectrum of the pure polymer film which has a clear absorption minimum at around 300 nm which is absent in the spectrum of the pure Flrpic film (Fig. S12 in ESI). A minimum at around 300 nm is clearly seen in the excitation spectrum. These observations are in contrast to the results of the corresponding experiments in solution described earlier and indicate that the extent of energy harvesting by poly(XOMA) is much greater in the solid state than in solution.

Energy transfer efficiency estimation was attempted for the film samples in the same manner as applied for the solution samples; however, accurate estimation was difficult due to the fact that emission intensity seems not to be completely proportional to the concentration of Flrpic, especially at a higher $\langle \text{Flrpic} \rangle$.

Effects of π -stacking on T_1 energies were investigated by DFT calculations at the B3LYP method using the 6-31G(d) basis set for a unimer, meso (m) and racemo (r) dimer, and mm, mr, and rr trimer models of poly(XOMA) (Fig. S13 in ESI). The m dimer and mm and mr trimers having tight, face-to-face π -stacked conformations before geometry optimization had much lower T_1 energies compared with the unimer with the largest difference being -1.92 eV while rr

trimer did not indicate a significant change in T_1 energy. Similar effects of stacking on lowest singlet excited (S_1) energies were observed. These results indicate that close stacking between adjacent units decreases excited energy. On the other hand, after optimization, the stacking of the poly(XOMA) models were much less tight, and effects of stacking on T_1 and S_1 levels became negligible, suggesting that in the real solution and film systems, the T_1 level of poly(XOMA) would be maintained high enough so energy harvesting to FIrpic is feasible.

T_1 level of poly(XOMA) was estimated by emission spectrum of the pure poly(XOMA) film to be 2.88 eV (a peak at 431 nm) (Fig. S14 in ESI). This value is lower than that of xanthone^{20,21} but is higher than that of FIrpic.⁹ The film indicated a weak, broad emission in the range of ca. 400-700 nm which is much broader than the emission of xanthone dispersed in PMMA (ca. 380-520 nm).²¹ These results suggest that the emission from the poly(XOMA) film is based on excimer in triplet excited states and that T_1 level is reduced by excimer formation.

In conclusion, Poly(XOMA) was synthesized as a polymer having a xanthone moiety in the side chain for the first time and its triplet energy harvesting ability was evaluated. Poly(XOMA-co-MMA) was also prepared and characterized. Poly(XOMA) appears to have a π -stacked conformation and poly(XOMA-co-MMA) a less ordered one. Poly(XOMA) exhibited triplet energy harvesting effects for blue phosphorescent FIrpic where the effects were far greater in the solid state than in a CHCl_3 solution. Poly(XOMA-co-MMA) also indicated harvesting effects in the solid state but the extent was lower than those of poly(XOMA). π -Stacked conformation thus plays an important role in triplet energy harvesting: energy migration among xanthone moieties in a chain would be facilitated by π -stacking.

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Notes and references

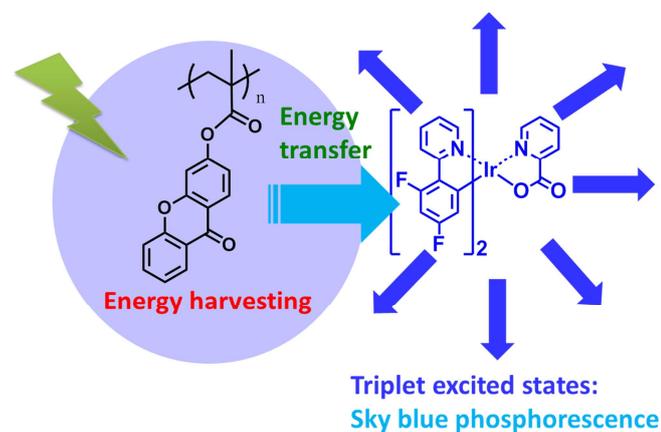
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† Electronic Supplementary Information (ESI) available: [Experimental details, spectrometric data of compounds, and film properties]. See DOI: 10.1039/c000000x/

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TOC graphic



Poly(xanthone-3-yl methacrylate) having a π -stacked conformation efficiently harvests photo excitation energy for sky blue phosphorescent emission of iridium bis[(4,6-difluorophenyl)pyridinato-N,C2]picolinate (FIrpic) in solution and in film.