Synthesis of Dual-Emissive Polymers Based on Ineffective Energy Transfer through Cardo Fluorene- Containing Conjugated Polymers

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KEYWORDS

Energy transfer, BODIPY, fluorene, conjugated polymer, dual emission, cardo structure, light-harvesting antennae

ABSTRACT

We describe here the design and synthesis of the conjugated polymers containing dye-modified cardo fluorenes for the dual emissions. Mono and di-substituted cardo fluorenes with boron dipyrromethene (BODIPY) were introduced into alternating conjugated polymers using bis-thienyl-benzothiadiazole as a comonomer for constructing the donor (D)-acceptor (A) pairs through the main-chains. The polymeric products showed good solubility in the common organic solvents and good film-formability. Strong emissions were obtained from the synthesized polymers in both solution and film states. In particular, multi-color emissions in green and red regions derived from each component were observed from the solutions containing the synthesized polymers. From the emission lifetime measurements, it was found that the energy transfer should be suppressed between the side and the main-chains, leading to the dual emission from the polymers. Furthermore, we also observed that the synthesized polymers have the light-harvesting antenna (LHA) effects and the color tunability by changing the number of BODIPY dyes tethered to the cardo fluorene.

INTRODUCTION

Dual-emissive polymers which show the two kinds of emissions from a single material in the different wavelength regions with the excitation at the single wavelength light are versatile not only for preparing optical devices but also for applying to the bio-sensors.¹ For instance, the white light-emissive materials which are applicable as an artificial illumination or a back light in the display were manufactured from the combination with the red, green, and blue chromophores.¹ By introducing these dyes into the polymers with or without covalent bonds, the multiple emission can be obtained, leading to the white-light emission for the human eyes. The emission colors were also tuned by the composition ratio. Dual emissions originated from the radiative transitions from the different excited states such as locally excited and charge transfer (CT) states² or singlet and triplet excited states³ were used as the sensing technology for the biomolecules. By comparing the intensities of each emission band, the detection was achieved for the base-pairing in DNA² and oxygen concentration³. To observe such dual emissions, the transitions from different excited states are essential with the suppression of the energy transferring between these energy states. However, it is often the case with the dyads, by connecting two kinds of fluorescent dyes closely, the energy transferring proceeds efficiently even though the overlapping of the spectra of the donor and the acceptor is very small, resulting in the single emission. Therefore, the elaboration on the molecular design for receiving each emission individually is necessary to obtain the dual emission with high efficiency.

We have reported the isolation effect from the electronic interaction by the cardo structure in polyfluorenes.⁴ It was shown that the influence of the electron-withdrawing and donating groups tethered to the polyfluorene via the cardo carbons can be completely inhibited. Therefore, the pure blue emissions were observed from a series of the modified polyfluorenes with various electron-positive and negative units. In addition, it was also presented that by tethering the fluorophores to polyfluorene via the cardo carbon, the concentration quenching can be avoided.⁵ Therefore, there is large possibility to realize the multi-functional emissive polymers based on the preprogrammed design without loss of

intrinsic optical properties of the components by undesired energy transfer or electronic interaction. Thus, we proposed that the cardo fluorene should be a versatile nanobuilding block for assembling the optically-functional molecules without loss of their functions. On the other hand, it is still unchallenged to control the energy transfer efficiency between the side chains and the polymer main-chains. Next goal is to establish the suppression of energy transferring with the side chains and receive the emissions individually from each component. In particular, we aim to realize the multi-emission based on the cardo structure-containing modified polyfluorene with emissive dyes by inhibiting the energy transfer between main and side chains.

Herein, we present the dual-emissive polymers involving the cardo fluorene structure. To suppress the energy transfer between the chromophore and the polymer, we employed the boron dipyrromethene (BODIPY) dye and the conjugated polymer composed of the D-A alternative structure because of the small overlapping of their emission and absorption spectra, respectively. A series of the modified cardo fluorene with single and dual BODIPY molecules were conjugated with a bis-thienyl-benzothiadiazole-containing acceptor unit, and the optical properties were evaluated. BODIPYs are well known as a versatile fluorophore in material science as well as biotechnology. However, it is often observed that optical properties of BODIPYs were critically spoiled by agglomeration because of the strong aggregation ability. In addition, most of the BODIPY-containing polymers also showed the loss of optical properties via the concentration quenching. In contrast, we observed the dual emissions in green and red regions originated from the BODIPY units and the D-A-type conjugated polymer moieties, respectively. Furthermore, we observed the synthesized polymers can possess the LHA effect and the color tenability by modulating the number of the substituted dyes via the cardo fluorene. Rational design for receiving multi-color emission from the single material is demonstrated.

Experimental section

General. ^1H , ^{13}C and ^{11}B NMR spectra were measured with a JEOL EX-400 (400 MHz for ^1H , 100 MHz for ^{13}C , 128 MHz for ^{11}B) spectrometer. Coupling constants (J value) are reported in Hertz. ^1H and ^{13}C NMR spectra used tetramethylsilane (TMS) as an internal standard. ^{11}B NMR spectra were referenced externally to $\text{BF}_3\cdot\text{OEt}_2$ (sealed capillary) in CDCl_3 . The number-average molecular weight (M_n) and the molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] values of all polymers were estimated by size-exclusion chromatography (SEC) with a TOSOH G3000HXL system equipped with three consecutive polystyrene gel columns [TOSOH gels: α -4000, α -3000, and α -2500] and ultraviolet detector at 40 °C. The system was operated at a flow rate of 1.0 mL/min, with CHCl_3 as an eluent. Polystyrene standards were employed for calibration. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer, and the absolute quantum yield was calculated by integrating sphere method on the HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer in chloroform. Fluorescence lifetime analysis was carried out on a HORIBA FluoreCube spectrofluorometer system; excitation at 375 nm was carried out using a UV diode laser (NanoLED-375L).

Materials. Tetrahydrofuran (THF), diethyl ether (Et_2O), and triethylamine (Et_3N) were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). 2,7-Dibromo-9,9-didodecylfluorene was obtained commercially, and used without further purification. 4,7-Bis-(3-hexylthiophen-2-yl)benzo[1,2,5]thiadiazole, monomers **1** and **2** were prepared according to the literature.⁵ All reaction was performed under argon atmosphere.

4,7-Bis[4-hexyl-5-(trimethylstannyl)thiophen-2-yl]benzo[c][2,1,3]thiadiazole (3). A THF solution of 2,2,6,6-tetramethylpiperidine (TMP) (1.5 mL, 8.8 mmol) was cooled to $-78\text{ }^\circ\text{C}$ and, *n*-butyllithium in

hexane (5.0 mL, 8.0 mmol, 1.6 M) was added. After the solution was allowed to warm until room temperature in 20 min, the resulting solution was cooled to $-78\text{ }^{\circ}\text{C}$, again. A solution of 4,7-bis-(3-hexylthiophen-2-yl)benzo[1,2,5]thiadiazole (1.62 g, 3.46 mmol) in THF (10 mL) was added and stirred for 30 min. Then, 1 M solution of trimethyltin chloride in hexane was added, and the reaction mixture was allowed to warm to room temperature. After stirring for 20 h, water was added, followed by extraction with cyclopentyl methyl ether (CPME). The mixture was washed three times with 0.1 M hydrochloric acid to remove TMP. After drying over MgSO_4 and removal of the solvent under vacuum, compound **3** (2.70 g, 98%) was obtained as a yellow solid after recrystallization in ethanol twice. ^1H NMR (CDCl_3 , ppm) δ 7.60 (s, 2H), 7.16 (s, 2H), 2.67 (t, $J = 8.2\text{ Hz}$, 4H), 1.68–1.56 (m, 4H), 1.31–1.12 (m, 12H), 0.81 (t, $J = 6.5\text{ Hz}$, 6H), 0.41 (s, 18H). ^{13}C NMR (CDCl_3 , ppm) δ 154.27, 142.88, 138.47, 138.01, 137.53, 129.49, 127.58, 31.54, 30.82, 29.23, 22.51, 18.43, 14.01, -8.14 . HRMS (p-MALDI) Calcd for $\text{C}_{32}\text{H}_{48}\text{N}_2\text{S}_3\text{Sn}_2$: m/z 796.10181; Found: m/z 796.10580.

Synthesis of polymer P1. A typical polymerization protocol via the Stille coupling reaction is shown here: A solution containing monomer **1** (91 mg, 100 μmol), **3** (79 mg, 100 μmol), $\text{Pd}_2(\text{dba})_3$ (1 mg, 1 μmol) and tri(2-furyl)phosphine (2 mg, 9 μmol) in 1 mL of anhydrous toluene was stirred at $100\text{ }^{\circ}\text{C}$ for 5 days under argon atmosphere. The resulting products were reprecipitated twice with a small amount of chloroform into 50 mL of methanol. Filtration gave a red solid (110 mg, 91%). ^1H NMR (CDCl_3 , ppm) δ 7.80 (2H), 7.71 (2H), 7.39 (4H), 7.51 (1H), 7.42 (2H), 7.34 (1H), 7.24 (2H), 7.19 (2H), 6.83 (2H), 3.93 (2H), 2.67 (4H), 2.50 (6H), 2.26 (4H), 1.76 (2H), 1.72 (4H) 1.42 (2H), 1.29 (20H), 1.21 (6H), 0.86 (15H). ^{13}C NMR (CDCl_3 , ppm) δ 158.27, 154.15, 153.61, 152.62, 146.96, 144.78, 142.99, 139.99, 139.24, 138.36, 134.33, 133.96, 132.61, 131.86, 130.78, 129.69, 129.18, 128.77, 128.38, 127.25, 125.70, 125.53, 123.27, 120.73, 114.54, 68.03, 64.94, 31.79, 31.55, 30.72, 29.65, 29.33, 29.28, 26.06, 22.63, 22.54, 17.07, 14.57, 14.06, 14.02, 12.44, 11.79, 11.72. ^{11}B NMR (CDCl_3 , ppm) δ 0.77.

Synthesis of polymer P2. Similarly to the preparation of **P1**, polymer **P2** was prepared from **2** (59 mg, 70 μ mol) and **3** (43 mg, 70 μ mol) in the presence of $\text{Pd}_2(\text{dba})_3$ (0.5 mg, 0.6 μ mol) and tri(2-furyl)phosphine (1.0 mg, 4 μ mol) in 92% yield as a red solid (70 mg). ^1H NMR (CDCl_3 , ppm) δ 7.84 (2H), 7.75 (2H), 7.65 (4H), 7.56 (2H), 7.44 (4H), 7.36 (2H), 7.23 (2H), 2.67 (4H), 2.50 (12H), 2.26 (8H), 1.65 (4H), 1.32 (12H), 1.12 (12H), 0.91 (12H), 0.81 (6H). ^{13}C NMR (CDCl_3 , ppm) δ 154.13, 153.76, 152.17, 145.95, 145.48, 144.67, 143.08, 139.63, 139.30, 138.26, 134.97, 134.77, 134.18, 132.88, 132.81, 131.96, 130.72, 129.74, 128.64, 128.58, 127.26, 126.06, 125.74, 125.60, 123.17, 120.90, 65.53, 31.52, 30.72, 29.62, 29.13, 22.52, 17.06, 14.57, 14.00, 12.43, 11.86. ^{11}B NMR (CDCl_3 , ppm) δ 0.78.

Synthesis of polymer P3. Similarly to the preparation of **P1**, polymer **P3** was prepared from 2,7-dibromo-9,9-didocyl-fluorene (66 mg, 100 μ mol) and **3** (79 mg, 100 μ mol) in the presence of $\text{Pd}_2(\text{dba})_3$ (1 mg, 1 μ mol) and tri(2-furyl)phosphine (2 mg, 9 μ mol) in ~100% yield as a red solid (100 mg). ^1H NMR (CDCl_3 , ppm) δ 7.74 (6H), 7.63 (2H), 7.42 (2H), 2.75 (4H), 2.06 (2H), 1.74 (2H), 1.19 (48H), 0.85 (10H), 0.70 (6H). ^{13}C NMR (CDCl_3 , ppm) δ 154.26, 151.75, 145.36, 142.99, 140.48, 133.18, 131.59, 129.67, 127.31, 125.31, 124.79, 120.03, 55.40, 40.57, 31.89, 31.61, 30.79, 30.07, 29.96, 29.75, 29.59, 29.31, 29.24, 23.82, 22.65, 22.58, 14.08, 14.05.

Results and discussion

In the design of the polymer with multiple emissions, the suppression of the energy transfer is mainly considered: We aimed to achieve the small overlapping in the spectra between the emission of the donor unit and the absorption of the acceptor unit. BODIPYs are a class of fluorophores with high quantum yields and light absorption ability.⁶ Especially, because of their intrinsic sharp absorption and emission spectra, the suppression of energy transfer with other kinds of organic dyes in the single material can be achieved, resulting in the white emission.⁷ The alternating polymers composed of the bithienylbenzothiadiazole unit are known as a low-band gap polymer and have been used as a conventional material in the opto-electric devices such as photovoltaic cells and electroluminescence devices.⁸ These polymers show the emission in the red region with the excitation light in the shorter-wavelength region than that of the emission of BODIPY originated from the strong D-A interaction. Based on these data, we selected the bithienylbenzothiadiazole unit as a comonomer. The design and synthesis of the polymers is outlined in Scheme 1. The dibromo fluorene monomers with the BODIPY units were synthesized according to the literature.⁵ All monomers were characterized by ¹H, ¹³C and ¹¹B NMR spectroscopies and mass measurements, and it was concluded that pure monomers with the desired structures were obtained.

Scheme 1

The polymerization via the Stille coupling reaction was executed as shown in Scheme 1. The products showed good solubility in common organic solvents such as chloroform, THF, and DMF and film-formability for the preparation of homogeneous films via casting or spin-coating methods. The polymer properties determined from the GPC analysis are shown in Table 1. The polymers **P1**, **P2** and **P3** were obtained as red solids in good yields (91–100%). The number-average molecular weights (M_n) and the

molecular weight distributions (M_w/M_n) of the polymers, measured by the size-exclusion chromatography (SEC) in chloroform toward polystyrene standards were from 4,700 to 17,000 with 1.6 to 1.9, respectively. In addition, the data for structural analysis by ^1H , ^{13}C and ^{11}B NMR were corresponded to those of the monomers. Thus, we concluded that the polymers should possess the designed chemical structures, and unintended conformation or aggregations were less obtained in the solutions.

Table 1

The electronic structures of the synthesized compounds at the ground states were evaluated. The synthesized polymers were dissolved in chloroform (1.0×10^{-5} M, monomer concentration), and UV-vis absorption measurements were performed (Figure 1). The results are listed in Table 2. **P1** and **P2** showed the significant absorption bands with the peaks at 370 nm attributable to π - π^* transition of fluorene and 530 nm originated from BODIPY.⁵ From the solution containing **P3**, the weak broad absorption band in the region 400–500 nm attributable to CT transition of the polymer main-chain was observed.⁸ Less peak shifts in the spectra were obtained from the polymers compared to that of **4**. In particular, the magnitudes of the absorption bands from BODIPYs in the polymers were corresponded to those of the model **4**. The molar extinct coefficients were simply represented as the sum of the number of BODIPYs in the single monomer unit in **P1** and **P2**. These data clearly indicate that the electronic interaction between the BODIPY dyes and the polymer main-chains should be suppressed. As observed in our previous reports, the cardo carbon plays a critical role in the isolation of conjugation systems at the ground states.^{4,5} The absorption spectra of the polymers were also investigated in the film states (Figure S2, Table S1). The thin films with the thickness of approximately 100 nm for the measurements were prepared by the spin-coating method with the chloroform solutions (1.0 mg/mL) of the polymers

on the quartz plate. From the microscopic observations, it was confirmed that all polymer films possess homogeneous states at the sub-micron order (Figure S5). The similar results were obtained from the film samples to the solution states. The isolation effects by the cardo carbon can be obtained even in the condensed states. These data suggest that the cardo fluorene should be a suitable platform for accumulating the optically-functional molecules without changing their intrinsic properties.

Figure 1, Table 2

The emission properties of the polymers were compared in chloroform to those of model systems, **M1** (a mixture of **P3** 1.0×10^{-7} M as the monomer concentrations and BODIPY (**4**) 1.0×10^{-7} M corresponding **P1**) and **M2** (a mixture of **P3** 1.0×10^{-7} M and compound **4** 2.0×10^{-7} M corresponding **P2**). The photoluminescence spectra were obtained with the excitation light at 465 nm as an absorption maximum of **P3** and 525 nm of **4**, respectively (Figures 2 and 3). **P3** exhibited the broad emission band with the peak around 630 nm between 540 nm and 780 nm originated from the CT transition. **M1** and **M2** samples showed strong emissions originated from both the BODIPY units and **P3**. Notably, the emission peaks originated from the BODIPY units were observed both in **P1** and **P2**. In particular, by changing the number of the BODIPY units tethered to the polymer main-chains, the emission intensity from the BODIPY units was varied. These results are the proof of concept to present the dual-emissive materials based on the cardo fluorene unit. The energy transfer from the BODIPY units in **P1** and **P2** to the polymer main-chain could be suppressed via the cardo fluorene units. From the film state, the strong emissions were observed with relatively good quantum yields in the red regions comparing to our previous results (Figure S3 and Table S1).⁶ It is assumed that the inter-chain energy transfer could efficiently occur in the condensed state.

The emission lifetime measurements were executed to evaluate the energy transfer efficiencies (Table 2). The energy transfer efficiencies could be calculated by the following equation (1), respectively.

$$E_{\text{eff}} = 1 - (I_{\text{DA}}/A_{\text{DA}}) / (I_{\text{D}}/A_{\text{D}}) = (1 - \tau_{\text{DA}}/\tau_{\text{D}} \cdot A_{\text{D}}/A_{\text{DA}}) = (1 - \Phi_{\text{DA}}/\Phi_{\text{D}} \cdot A_{\text{D}}/A_{\text{DA}}) \quad (1)$$

where I_{DA} is a fluorescence intensity of donor (the BODIPY units) in the presence of acceptor (the polymer main-chains) and I_{D} in the absence of acceptor, A_{DA} is an absorption of donor in the presence of acceptor and A_{D} in the absence of acceptor, τ_{DA} is a fluorescence lifetime of donor in the presence of acceptor and τ_{D} in the absence of acceptor, Φ_{DA} is a quantum yield of donor in the presence of acceptor and Φ_{D} in the absence of acceptor. The absorptions were determined from the subtraction of the spectra. Because the emission bands of the polymer main-chain and the BODIPY unit were overlapped, each of the donor and the acceptor fluorescence decay and quantum yield were unable to be determined precisely. Therefore, E_{eff} was calculated by fluorescence intensity only in emission region of the BODIPY unit. According to eq 1, the values of E_{eff} were evaluated as 95% from **P1** and 73% from **P2** by using the observed intensity of the emission maxima in the models and the polymers, respectively. These values are relatively lower than those of the D-A dyads with the covalent bond in close proximity.⁹ These data represent the energy transfer should be suppressed via the cardo structure. These results present that the cardo fluorene can work as a nanobuilding block for assembling the chromophore with the suppression of unexpected electronic interaction.

Table 2

It was often observed from the previous reports that the emission quantum yields of BODIPYs readily decreased because of the concentration quenching in the materials.⁷ On the other hand, the quantum yields of the BODIPY units were maintained in the polymers (Table 2). Finally, the apparent emission intensity increased by increasing the number of BODIPYs. The emission bands from the polymer main-chains of **P1** and **P2** in the region around 630 nm with the excitation light at 465 nm were approximately 1.25-times larger than that of **P3**. These results indicate that the BODIPY units in the polymers work as an LHA.⁵ By changing the excitation wavelength, the LHA effect increased significantly. With the excitation light at 525 nm, the emission intensities of **P1** and **P2** were enhanced 12 and 19 times larger than that of **P3**, respectively (Figure 3). The emissions of the BODIPY units were still observed with strong intensity showing dual emissions. The tuning of emission colors was accomplished after the amplification (CIE 1976 $\mu = 0.3684$, $\nu = 0.5433$ in **P1** and $\mu = 0.2815$ $\nu = 0.5562$ in **P2**, Figure 4). These data clearly indicate that the cardo fluorene-based molecular assembly could have various advantages such as LHA effect, color tuning, as well as multiple emissions.

Figure 4

Conclusion

The design and the proof of this concept for dual-emissive polymers involving the cardo fluorene structure are presented. Based on the strategy for the suppression of the energy transfer between the chromophore and the polymer composed of the D-A alternative structure utilizing the cardo structure, the dual emission was obtained. Our study includes three significant issues: Multi-color emissive polymers were presented from the single polymer. Moreover, the products showed good solubility in the common solvents. Crucial phase separation or agglomeration even at the molecular levels could be suppressed. Furthermore, the main-chain conjugation which is an essential factor for realizing high carrier ability would be maintained in the final products. These advantages are feasible for manufacturing advanced opto and/or electronic devices with low costs via the printing methods. Secondly, our polymers are composed of the common units in the conjugated polymers such as BODIPY, fluorene, thiophene and benzothiadiazole. Some of them are commercially available. The materials can be prepared without specialized conditions. Especially, it is expected that our concept could be applicable widely for the design to fabricate multi-color emissive products from conventional materials. Thirdly, the synthesized polymers have the tunability of the optical properties. We can modulate the emission color by changing the number of the BODIPY units tethered to the cardo fluorene. In addition, the LHA effect was obtained. It can be expected that multiple functions including dual emissions could be readily realized based on the cardo fluorene-based polymers.

Acknowledgements

This work was partially supported by Izumi Science and Technology Foundation (for K.T.), "the Adaptable and Seamless Technology Transfer Program" through target-driven R&D, Japan Science and Technology Agency (JST) and a Grant-in-Aid for Scientific Research on Innovative Areas "New Polymeric Materials Based on Element-Blocks (No.2401)" (24102013) of The Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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Scheme 1. Synthesis of the polymers

Reagents and conditions: a) $\text{Pd}_2(\text{dba})_3$, tri(2-furyl)phosphine, toluene, 100 °C, 5 d.

Table 1. Polymerization results

Polymers	Yield (%) ^a	M_n^b	M_w/M_n^b	DP ^c
P1	91	17,000	1.85	28
P2	92	4,700	1.78	6.8
P3	~100	12,000	1.64	24.2

^a Isolated yields after precipitation.

^b Estimated by size-exclusion chromatography (SEC) based on polystyrene standards in chloroform.

^c Degree of polymerization estimated by number-average molecular weight.

Table 2. Photophysical properties of the polymers in solution state

Compound	$\lambda_{\text{abs,max}}$ [nm] ^a	$\lambda_{\text{PL,max}}$ [nm] ^b	Φ_{PL} ^c	E_{eff} ^d	τ [ns] ^e	χ ^e	τ [ns] ^f	χ ^f	E_{LHA} ^g
P1	368 (60300), 527 (94600)	539, 625	0.37	0.95	3.28	1.190	2.82	1.162	12
P2	366 (52000), 528 (140500)	539, 620	0.40	0.73	3.43	1.288	3.50	1.180	19
P3	368 (49500), 466 (27000)	628	0.39	–	–	–	3.42	1.129	1
4	377 (8100), 527 (76500)	538	0.68	–	4.99	1.013	–	–	–

^a Evaluated in chloroform (1.0×10^{-5} M). (molar extinction coefficient).

^b Excited at 525 nm in chloroform (1.0×10^{-7} M).

^c Absolute quantum yield.

^d Energy transfer efficiency.

^e Photoluminescence lifetimes of the polymers on emission wavelength 540 nm in chloroform (1.0×10^{-7} M).

^f Photoluminescence lifetimes of the polymers on emission wavelength 625 nm in chloroform (1.0×10^{-7} M).

^g LHA efficiency compared to **P3**.

Figure 1. UV–vis spectra of the polymers and model systems in chloroform (1.0×10^{-5} M).

Figure 2. Photoluminescence spectra of the polymers (1.0×10^{-7} M) and the mixtures (**M1**, **4** and **P3** 1.0×10^{-7} M; **M2**, **4** 2.0×10^{-7} M, **P3** 1.0×10^{-7} M) in chloroform (excitation wavelength 465 nm).

Figure 3. Photoluminescence spectra of the polymers (1.0×10^{-7} M) and the mixtures (**M1**, **4** and **P3** 1.0×10^{-7} M; **M2**, **4** 2.0×10^{-7} M, **P3** 1.0×10^{-7} M) in chloroform (1.0×10^{-7} M, excitation wavelength 525 nm).

Figure 4. CIE 1976 diagram of the polymers.

Graphical Abstract