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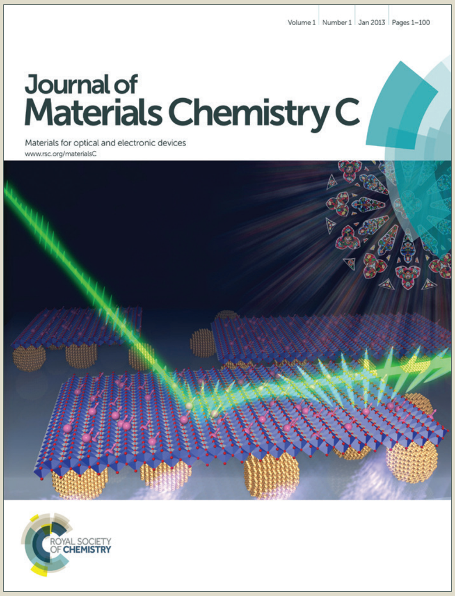

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Rigidity-Induced Emission Enhancement of Network Polymers Crosslinked by Tetraphenylethene Derivatives

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In this paper, we prepared various network polymers with crosslinkers having two or four acryloyl groups derived from AIE luminogen, and investigated the relationship between rigidity of network polymer and emission behaviour. The crosslinkers showed representative the AIE property. A conventional radical polymerization with various vinyl monomers produced corresponding network polymers. The variation of vinyl monomers or the crosslinkers allowed us to obtain network polymers with different rigidity. Fluorescence spectroscopy of the network polymers revealed rigidity dependent emission enhancement accompanying hypsochromic shift. In addition, the network polymer showed temperature and solvent dependent emission behaviour. The crosslinker with less crosslinkable substituents showed higher susceptibility toward the environment such as rigidity, temperature, and solvent.

Introduction

Aggregation-induced emission (AIE) characteristics have recently emerged as a novel class of fluorescent materials in the last decade.[1-9] Molecules exhibiting AIE characteristics are non-emissive in dissolved state, and drastically enhance their emission intensity in aggregated state. This is an exact opposite phenomenon of aggregation-caused quenching (ACQ), which is often found in general organic fluorescent molecules showing noticeable fluorescence in a diluted solution. Compared with general organic fluorescent molecules, the fascinating property of AIE luminogen has prompted chemists to develop application for such as fluorescent sensors,[10-13] biological probes,[14-17] and lighting devices[18-22], in a bulk or a concentrated state.

The systematic studies on AIE luminogen revealed that the restriction of intramolecular motion (RIM) of the molecule is primarily responsible for AIE phenomenon. The simplest way to express AIE property is to form an aggregation in a poor solvent via a reprecipitation process. However on deep consideration for the mechanism of AIE phenomenon, we can suppose that aggregate formation is not always necessary for it. In other words, aggregate formation should not be a requirement for AIE phenomenon, but just a sufficient condition for it, and other ways to suppress the molecular motion will be also able to trigger AIE phenomenon. This idea has been realized in the last year by utilizing supramolecular interaction to suppress the molecular motion of AIE luminogen.[23-25] For examples, Shinkai and coworkers presented "cyclization-induced emission (CIE)" driven by complexation between dicarboxylic acid and a tetraphenylethene (TPE) derivative, a representative AIE luminogen, tethering zinc-dipicolylamine groups in homogeneous buffer solution.[23] Song et al. reported emerging fluorescence via complexation between a TPE derivative and γ-cyclodextrin (γ-CD) in homogeneous solution.[24] Wu et al. reported fluorescence occurrence induced by anion coordination of TPE derivative having bisurea moieties.[25]

We recently reported a class of network polymer system crosslinked by an AIE luminogen, to control the emission behaviour derived from AIE crosslinker via interaction of the crosslinking point and the polymer chain.[26-28] A crosslinker in a network polymer is randomly fixed in the network, due to random crosslinking reaction. Therein, interaction between the crosslinking point and the polymer chain play a crucial role for the emission behaviour, without any aggregate formation. From this viewpoint, we have achieved the preparation of stimuli-responsive fluorescent hydrogel and elastomer crosslinked by AIE luminogen, and their emission behaviour responsible toward swelling degree, salt concentration, solvent, or temperature.[27-29] These findings motivated us to disclose the relationship of emission behaviour and rigidity of network polymers via systematic studies varying the polymer chain. In this research, we synthesized two crosslinkers tethering acryloyl groups derived from AIE luminogen based on TPE, and prepared network polymers from the crosslinkers and various vinyl monomers. And we investigated the relationship between rigidity of network polymer and emission efficiency.

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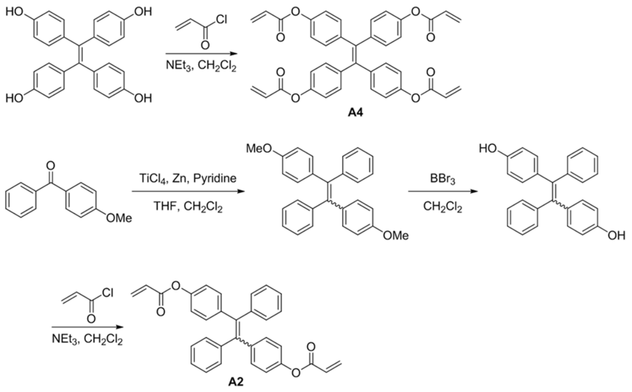
Electronic Supplementary Information (ESI) available: Experimental detail, DSC chart, and solvent dependent fluorescence spectra of the obtained network polymers are given. See DOI: 10.1039/x0xx00000x



Scheme 1. Preparation of crosslinkers **A4** and **A2**.

Results and discussion

The AIE-active acryl cross-linkers **A4** and **A2** were prepared as shown in Scheme 1. The tetraphenylethylene (TPE) moiety, which shows AIE property, was synthesized via homo McMurry coupling of 4,4'-methoxy benzophenone or 4-methoxy benzophenone, respectively, referring similar method previously reported.30 Demethylation of the methoxy groups and following esterification reaction with acrylic chloride afforded **A4** or **A2** in modest yield (see ESI). The obtained compounds were purified by silica gel column chromatography and characterized by ^{1}H NMR, IR, and high-resolution mass spectroscopies. The spectral data resulted in good agreement with their chemical structures. In ^{1}H NMR spectra, these compounds showed distinctive peaks at around 6.00~5.00 ppm derived from the acryloxy group, which is necessary for the succeeding radical polymerization.

To elucidate the optical properties of **A4** and **A2**, UV-Vis absorption and fluorescence spectra were evaluated as shown in Fig. 1. In the UV-Vis absorption spectra (10 μM acetonitrile solution, bold line), the absorption maximum (λ_{max}) appeared at 318 nm with high molar extinction coefficient (ε = 15000 M-1cm-1), indicating π→π* transition in the TPE unit.^{24} In a poor solvent (acetonitrile/H_2O = 1/99 (v/v), thin line), the absorption maximum was shifted to longer wavelength region (λ_{max} = 335 nm), due to the aggregation formation, whereas the spectral shape remained its original feature observed in a good solvent. The crosslinkers **A4** and **A2** themselves showed almost identical absorbing features, irrelevant to the number of acryloxy substituents. In the fluorescence measurement, **A4** and **A2** exhibited inherent AIE properties. In dissolved state in a good solvent such as acetonitrile, they exhibited a trivial emission at around 480 nm. On the other hand, the aggregation originated from the addition of H_2O clearly increased the emission intensities (solid line, acetonitrile/H_2O = 20/80) with its maximum at around 473 nm (**A2**) and 471 nm (**A4**), respectively. In a mixed solvent of acetonitrile/H_2O = 1/99, the emission intensities became more than 200 times compared to those in dissolved state. These results implied that crosslinkers **A4** and **A2** can act as both a cross-linker in conventional radical polymerization and AIE luminogen.

The samples of network polymers were prepared via conventional radical polymerization process initiated by AIBN and following monomers, methyl acrylate (**MA**), ethyl acrylate (**EA**), butyl acrylate (**BA**), methyl methacrylate (**MMA**), butyl methacrylate (**BMA**), and styrene (**St**) as shown in Scheme 2. The monomer and the crosslinker (**A4** or **A2**) were dissolved in DMF, and the reaction solution was kept standing at 60 °C for 24 hours in a Teflon® mold (see ESI for detail). The ratio of monomer and crosslinker was arranged according to 0.8 mol% for the each vinyl group, thus 0.2 mol% for **A4** and 0.4 mol% for **A2**, and 1.0 mol% of AIBN to monomer was employed. After immersion in DMF for purification, the obtained film sample was dried under vacuum at 40 °C. These results indicated **A4** and **A2** successfully functioned as an AIE crosslinker in radical polymerization process, comparable to a conventional crosslinker.

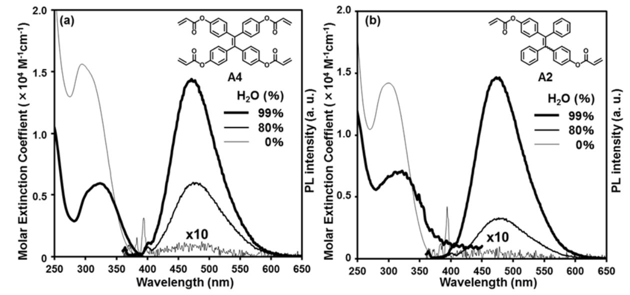
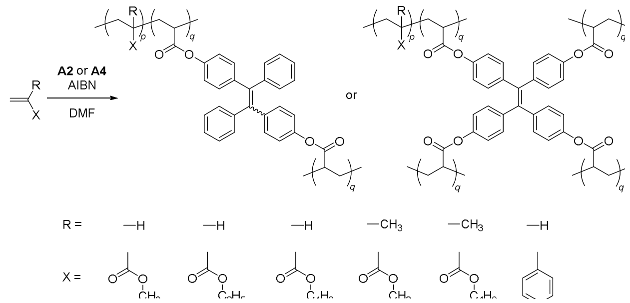


Fig. 1 UV-vis absorption and fluorescence spectra of crosslinkers (a) **A4** and (b) **A2** in CH_3CN/H_2O with various mixing ratio.



Scheme 2. Preparation of network polymers with crosslinkers **A4** and **A2**.

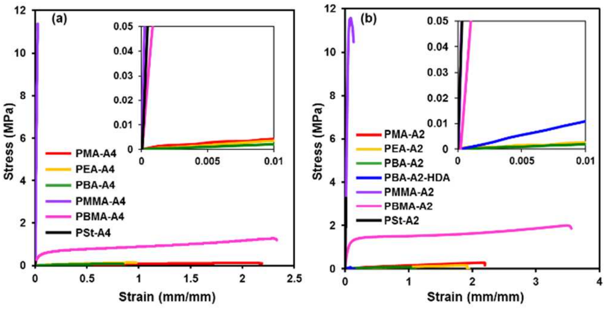


Fig. 2 Stress-strain curves measured at room temperature for the obtained network polymers from crosslinkers (a) **A4** and (b) **A2**.

To obtain a deep insight of rigidity in these network polymers, tension experiment was carried out to determine strain-stress curve and Young's modulus (*E*) (Fig. 2 and Table 1). Young's moduli of the network polymers varied depending on the polymer chain, rather than the crosslinker. Either **A4** or **A2** was employed for the crosslink, **MA**, **EA**, and **BA** showed low *E* value (< 0.3 MPa), while MMA and St showed high E value (> 200 MPa), BMA showed medium value (~ 5 MPa). These values are in good agreement with those of the reported linear polymers without crosslinking.[31] Addition of ten equivalents of another crosslinker 1,6-hexanediol diacrylate (**HDA**) to **A2** successfully enhanced the rigidity of sample (**PBA-A2-HDA**, Table 1). These data suggested that rigidity of the network polymers can be easily tuned by changing the polymer chain or the amount of crosslinker.

Table 1. Mechanical properties of the obtained network polymers.[a]

Sample	Max. Strain (mm/mm)	Max. Stress (MPa)	Young's Modulus *E* (MPa)
PMA-A4	2.18	0.11	0.12
PEA-A4	0.97	0.14	0.24
PBA-A4	0.83	0.085	0.17
PMMA-A4	0.024	11.4	469.5
PBMA-A4	2.30	1.27	2.22
PSt-A4	0.0025	0.16	N.D.[b]
PMA-A2	2.19	0.28	0.25
PEA-A2	1.90	0.16	0.12
PBA-A2	1.02	0.090	0.16
PBA-A2-HDA[c]	0.086	0.068	0.77
PMMA-A2	0.090	11.6	214.4
PBMA-A2	3.49	1.99	5.71
PSt-A2	0.011	2.56	248.5

[a] Measured at room temperature with a 10 mm/min of tension rate. [b] Not determined because the sample was to brittle. [c] The sample was prepared from **BA**, **A2** and **HDA** (10 eq. to **A2**) to enhance the rigidity.

To clarify the relationship between rigidity and emission behaviour of the obtained network polymers, fluorescence spectroscopy were conducted at room temperature as a bulk film. As shown in Fig. 3, the network polymers showed moderate emission derived from the TPE moiety in crosslinking point. Apparently, the crosslinking points are uniformly dispersed in the network polymer, thus the emission should originate from suppression of molecular motion of TPE by polymer chains around the crosslinking point, not by crosslinker aggregation. As the result, different emission was observed depending on the kind of crosslinkers **A4** and **A2** or monomers as summarized in Table 2. In samples from **A4**, the emission maxima stayed within 10 nm (from 446 nm (**PMA-A4**) to 455 nm (**PBA-A4**)), which was hypsochromically shifted compared to the aggregated state of **A4** alone (471 nm) in CH_3CN/H_2O (1/99, v/v). On another front, the samples from **A2** exhibited emission maxima ranging from 457 nm (**PMMA-A2**) to 482 nm (**PBA-A2**), while the emission maxima of aggregated state of **A2** was observed at 473 nm in CH_3CN/H_2O (1/99, v/v). These fluorescence spectra suggest that the substituent number of the crosslinkers (4 or 2) affects the emission wavelength to variation of polymer chains ($\Delta\lambda_{A4}$: 9 nm, $\Delta\lambda_{A2}$: 25 nm), thus samples from **A4** possess lower susceptibility to the polymer chain variation, due to more connecting polymer chains at the crosslinking point. In general, AIE luminogens show emission at longer wavelength in amorphous state, whereas they show emission at shorter wavelength in crystalline state, due to the difference in planarity and mobility in the two state.[32-34] This mechanism should be also responsible for our results, thus the planarity and mobility of TPE crosslinker were affected by the kind of monomer or the structure of crosslinker.

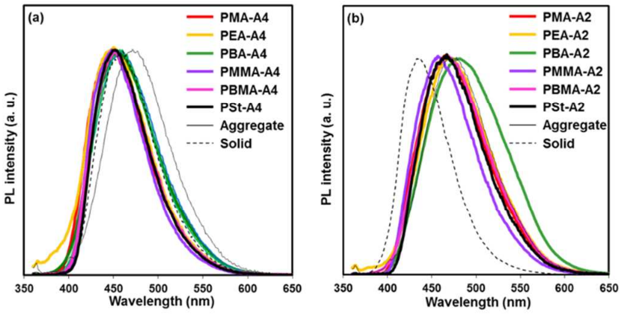


Fig. 3 Fluorescence spectra of aggregate (dispersed in CH_3CN/H_2O = 1/99), crystalline solid, and network polymers from crosslinkers (a) **A4** and (b) **A2**. Excitation wavelength = 350 nm.

Table 2. Emission behaviour of the obtained network polymers.

PX-An	A4			A2		
	E (MPa)[a]	λ_{em} (nm)	QY[b]	E (MPa)[a]	λ_{em} (nm)	QY[b]
PMA	0.12	446	0.53	0.25	466	0.43
PEA	0.24	450	0.48	0.12	470	0.38
PBA	0.17	455	0.44	0.16	482	0.28
PMMA	469.5	448	0.63	214.4	457	0.52
PBMA	2.22	451	0.56	5.71	467	0.38
PSt	-	452	0.59	248.5	467	0.54

[a] Young's modulus. [b] Absolute fluorescence quantum yield measured by using an integral sphere. [c] Measured in a mixed solvent of CH_3CN/H_2O (1/99, v/v). [d] Crystalline solid after removal of good solvent.

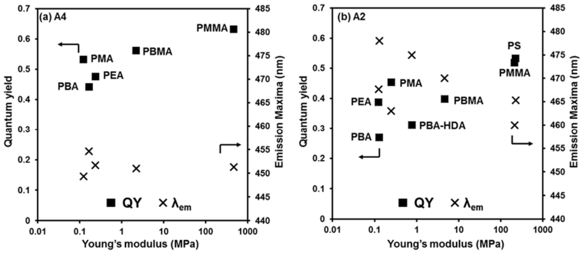


Fig. 4 Relationships between emission behaviour and rigidity of the obtained network polymers from (a) **A4** and (b) **A2**. Square represents fluorescence quantum yield, and cross represents emission maxima.

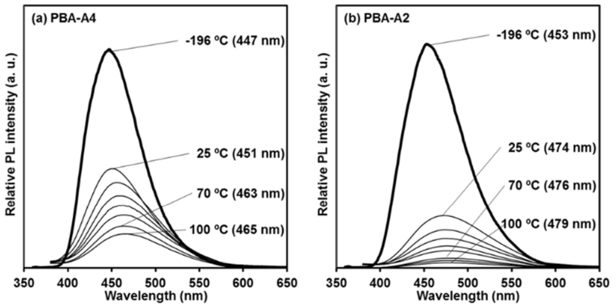


Fig. 5 Temperature dependent fluorescence spectra of (a) **PBA-A4** and (b) P**BA-A2**. The spectra at -196 °C (bold line) were measured in liquid nitrogen, and the others were measured in a temperature controller. In the parenthesis, emission maxima are shown. Excitation wavelength = 350 nm.

The relationships between emission behaviour and rigidity of the obtained network polymers were investigated as shown in Fig. 4 and Table 2. The elevation of Young's modulus (E) of the sample gradually increases its QY. For examples of a series of the samples from **A4**, QY in **PBA-A4** (E = 0.17 MPa) was 0.44, which increased to 0.56 in **PMMA-A4** (E = 469.5 MPa) and 0.59 in **PSt-A4** (E was not determined because of the brittleness). For samples from **A2**, QY in **PBA-A2** (E = 0.16 MPa) was 0.28, which increased to 0.54 in **PMMA-A2** (E = 248.5 MPa). In addition, **PBA-A2-HDA**, a reinforced sample of **PBA-A2**, showed higher QY (0.32) than that of **PBA-A2**. The study on fluorescence quantum yield also suggests that the structure of crosslinker influences on the response of emission efficiency to variation of polymer chains (ΔQY_{A4} : 0.19, ΔQY_{A2} : 0.26), thus the samples from **A2** also exhibit higher susceptibility to the polymer chain variation. We additionally prepared other samples employing non-crosslinking AIE monomer **A1** and crosslinker HDA (0.4 mol% to the monomer), thus **PBA-A1**, **PBMA-A1**, and **PMMA-A1**. They showed similar tendency with those of samples from **A4** and **A2** (see Experimental Section and Table S1). These findings indicate that the elevation of rigidity of the sample by changing the polymer chains increases its fluorescence quantum yield and induces hypsochromic shift of emission maxima, and the susceptibility of these photophysical properties can be tuned by changing the structure of crosslinker, that is, the substituent number of the crosslinker.

To attest the prominent stimuli-responsive emission behaviour, temperature dependent fluorescence spectra of the obtained network polymers was evaluated by using the most floppy samples from PBA as shown in Fig. 5. **PBA-A2** exhibited substantial decrease of emission intensity to 10% with increasing temperature from 25°C to 100 °C accompanying with slight bathochromic shift (474 nm → 479 nm), while **PBA-A4** showed modest decrease of emission intensity to 30% with large bathochromic shift (451 nm→ 465 nm). On the other hand in a cooling process, both samples exhibited similar emission with similar fluorescence quantum yield at -196 °C (**PBA-A4** : 447 nm, QY = 0.97, **PBA-A2** : 453 nm, QY = 0.94). At -196 °C, the molecular motion of AIE luminogen at the crosslinking point is equally suppressed to show similar emission behaviour, while it was released at upper temperature. For the susceptibility of emission intensity toward temperature, **PBA-A2** showed higher performance in a whole range of measurement temperature. On another front for the susceptibility of emission wavelength toward temperature, **PBA-A4** showed higher performance at above 25 °C. This result is probably caused by the difference of responding temperature range between **PBA-A2** and **PBA-A4** due to the structural difference at the crosslinking point. Indeed, **PBA-A2** higher susceptibility of emission wavelength toward temperature at below 25 °C. These observations indicated that the susceptibility of emission intensity and wavelength toward temperature can be also controlled by changing the structure of crosslinker.

Molecular motion around the crosslinking point in network polymers is also tuned by swelling of them in organic solvent. Therefore we next assessed transition of emission behaviour of the obtained network polymers upon immersion in good solvent, THF. As the result, **PBA-A2** showed drastic decrease of emission intensity within 60 min to 8% without any shift of emission wavelength, whereas that of **PBA-A4** exhibited drastic bathochromic shift of 17 nm with modest decrease of emission intensity (Fig. 6). The decrease of emission intensity upon immersion in THF was also evaluated by absolute fluorescence quantum yield (QY) as shown in Fig. S2a. Even after 60 min, **PBA-A4** exhibited moderate QY as 0.12, while that of **PBA-A2** reached 0.005. These differences also come from the mobility of the AE luminogen at the crosslinking point; i.e., molecular motion around **A4** are strictly hindered due to four crosslinkable substituents irrelevant to the mobility of polymer chain, while that around **A2** are mainly influenced by the mobility of polymer chain, because the AIE luminogen are more exposed to the network polymer chain matrix.

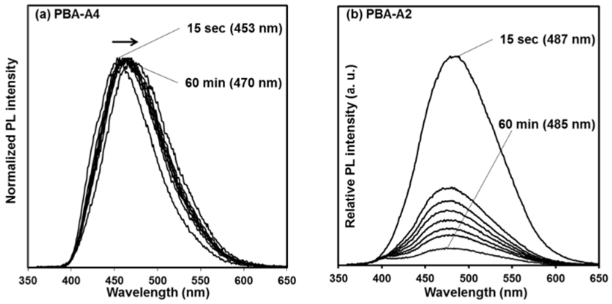


Fig. 6 Fluorescence spectra of (a) **PBA-A4** and (b) **PBA-A2** upon immersion in good solvent (THF) to 60 min. Excitation wavelength = 350 nm.

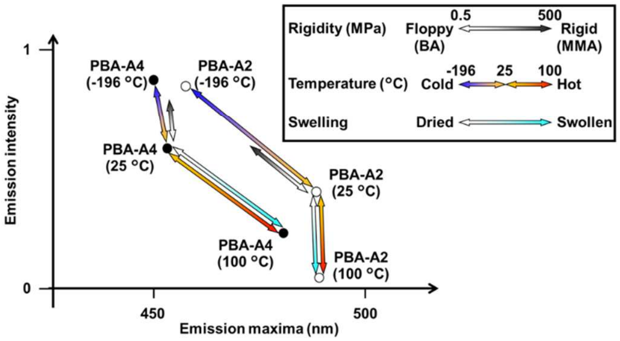


Fig. 7 Summary of emission behaviour of obtained network polymers in response to rigidity, temperature, and solvent.

The solvent-dependent emission behaviour of **PBA-A4** was additionally investigated. In THF, a good solvent for **PBA-A4**, it showed a high swelling degree as 9.31, on the contrary in a poor solvent as methanol, the swelling degree dropped to 1.42. Upon this change in swelling degree, the QY and emission maxima are also switched at least three times as shown in Fig. S2b. By changing the swelling solvent, the swelling degree was finely controlled, and the emission maxima showed gradual bathochromic shift with increase of the swelling degree (Fig. S3). These data suggested the possibility of emission colour control by changing the swelling solvent for network polymers.

Conclusions

In this research, we reported the preparation of various network polymers with crosslinkers tethering two or four acryloyl groups derived from AIE luminogen, and proved the relationship between rigidity of the network polymer and the emission behaviour of AIE luminogen at the crosslinking point. A conventional radical polymerization with various vinyl monomers provided corresponding network polymers. As a result, network polymers with different rigidity was obtained by varying the kind of vinyl monomers or the crosslinkers. The rigidity dependent emission enhancement accompanying hypsochromic shift was revealed fluorescence spectroscopy. The mobility of network polymer was controlled by temperature and solvent, and the emission behaviour also depended on them. The crosslinker with less crosslinkable substituents showed higher susceptibility toward the environment such as rigidity, temperature, and solvent. In our experiment, we successfully found the method to preciously control the emission from the AIE luminogen in network polymers as shown in Fig. 7. The combination of network polymer and AIE luminogen will open a new frontier for material chemistry, such as smart soft materials or sensing materials.

Acknowledgements

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Graphical Abstract for Table of Contents (TOC)

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

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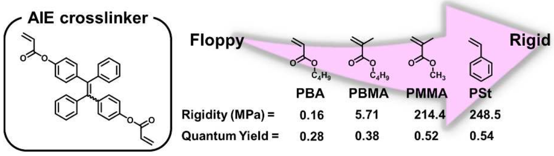

The network polymers crosslinked by molecules with aggregation-induced emission (AIE) property exhibited rigidity-induced emission enhancement derived from restriction of intramolecular motions.