Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for

Poly(dimethylsiloxane) and oligo(dimethylsiloxane) solvent effects on aromatic donor-acceptor interactions

Shogo Amemori, *[a,b,c] Kyoka Kikuchi, [d] and Motohiro Mizuno*[a,b,c]

[a]Nanomaterials Research Institute(NanoMaRI), Kanazawa University, Kanazawa 920-1192, Japan

[b]Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa 920-1192, Japan

[c]Institute for Frontier Science Initiative, Kanazawa University, Kanazawa 920-1192, Japan

[d]School of Chemistry, College of Science and Engineering, Kanazawa University, Kanazawa 920-1192, Japan

E-mail: amemori@stuff.kanazawa-u.ac.jp; mizuno@se.kanazawa-u.ac.jp.

1. Experimental Section

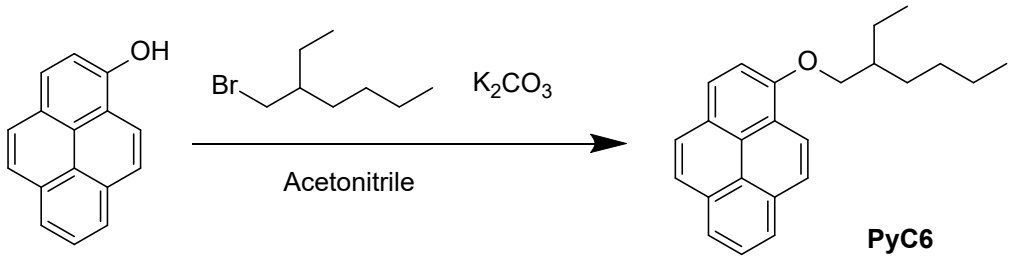
Instrumentation

^{1}H and ^{13}C NMR measurements were recorded on a Bruker Avance Neo 400 instrument (^{1}H 400 MHz and ^{13}C 100 MHz). UV/Vis spectra were recorded on a JASCO V-750 spectrometer with a JASCO ETCS-761 temperature controller. Fluorescence spectra were measured by using a Hitachi F-2500 fluorescence spectrophotometer. Elemental analysis and FAB mass spectroscopy were performed at the Research Institute for Instrumental Analysis, Advanced Science Research Center, Kanazawa University.

Materials.

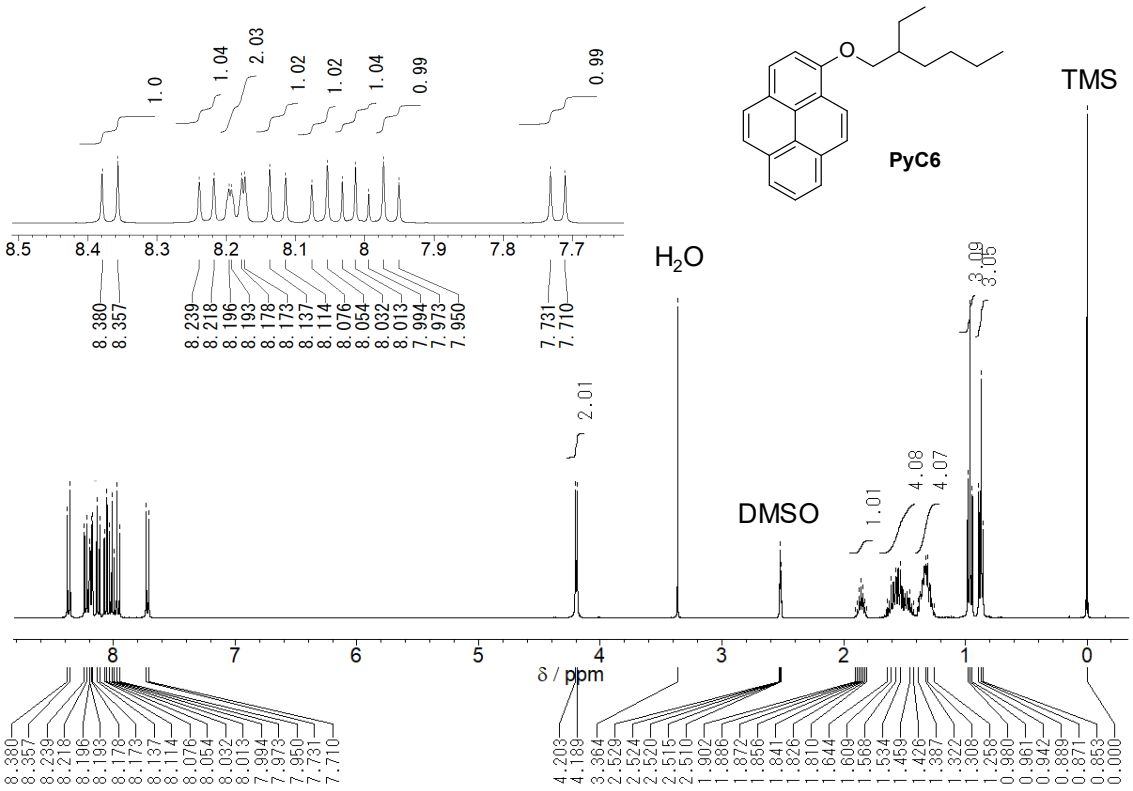
All reagents and solvents for synthesis and measurement were used as received without further purification. **PMDIC6** and compound **1** were synthesized according to the literature.[1,2]

Synthesis of **PyC6**

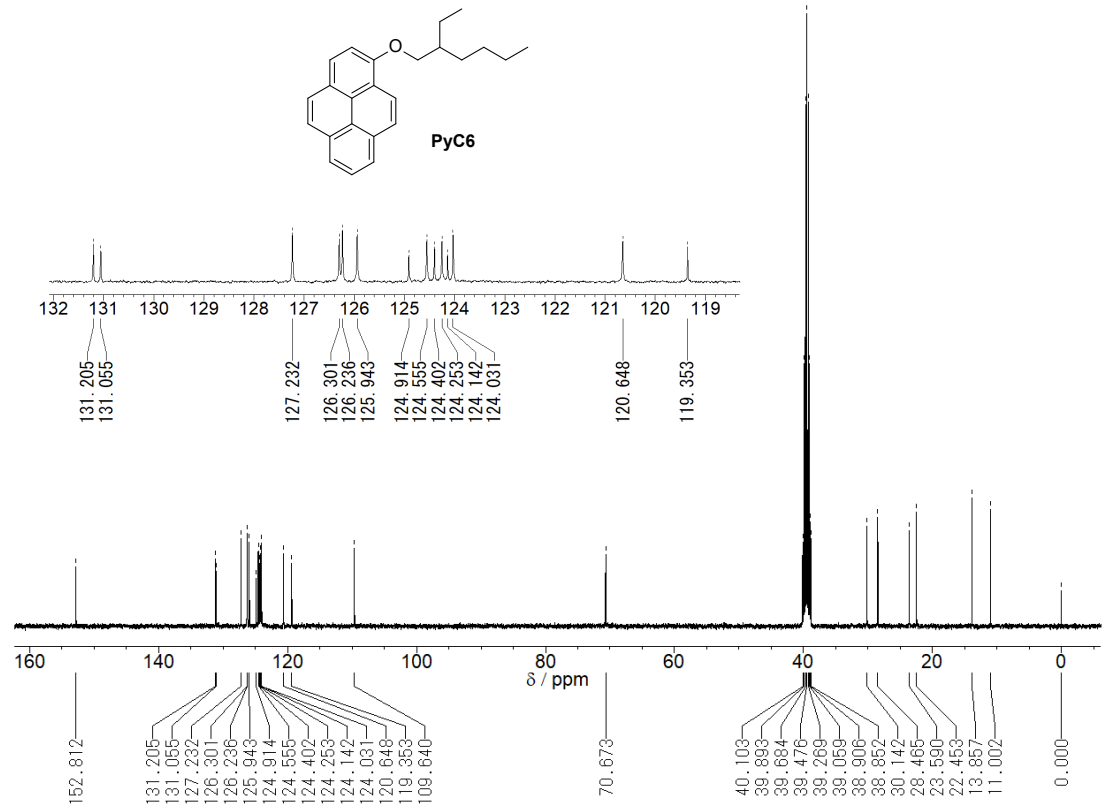


Under N_2, the mixture of 1-hydroxypyrene (1.00 g, 4.6 mmol) and K_2CO_3 (2.53 g, 18.3 mmol) and 1-bromo-2-ethylhexane (1.77 g, 9.2 mmol) and dry acetonitrile (40 mL) was stirred at 80 °C for 12 hours as monitored by TLC. The resulting mixture was cooled to the room temperature and poured into water (200 mL) and then extracted with CH_2Cl_2 (250 mL). The organic layer was washed with water, and dried over anhydrous Na_2SO_4, followed by evaporation to dryness. The residue was purified by silica gel column chromatography (CH_2Cl_2/Hexane=1/19) to obtain **PyC6** as a pale green oil (1.30 g, 3.9 mmol, 86%).

^{1}H NMR (400 MHz, DMSO-d_6, TMS standard): δ (ppm) 0.87 (t, J = 7.2 Hz, 3 H, CH_3), 0.96 (t, J = 7.6 Hz, 3 H, CH_3), 1.22-1.40 (m, 4 H, CH_2), 1.42-1.68 (m, 4 H, CH_2), 1.86 (sep, J = 6.1 Hz, 1 H, CH), 4.20 (d, J = 5.6 Hz, 2 H, CH_2), 7.72 (d, J = 8.4 Hz, 1 H, ArH), 7.96 (d, J = 9.2 Hz, 1 H, ArH), 8.01 (t, J = 7.6 Hz, 1 H, ArH), 8.07 (d, J = 8.8 Hz, 1 H, ArH), 8.13 (d, J = 9.2 Hz, 1 H, ArH), 8.16-8.21 (m, 2 H, ArH), 8.23 (d, J = 8.4 Hz, 1 H, ArH), 8.37 (d, J = 9.2 Hz, 1 H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6, TMS standard): δ (ppm) 11.00, 13.86, 22.45, 23.59, 28.47, 30.14, 38.91, 70.68, 109.64, 119.36, 120.65, 124.03, 124.14, 124.26, 124.40, 124.56, 124.92, 125.95, 126.24, 126.30, 127.23, 131.06, 131.21, 152.81. HRMS(FAB) Calcd for $C_{24}H_{27}O$ [$(M+H)^+$]: m/z 331.2062, Found: m/z 331.2060. Elemental analysis: calculated for $C_{24}H_{26}O$: C 87.23, H 7.93, Found: C 87.07, H 7.92.

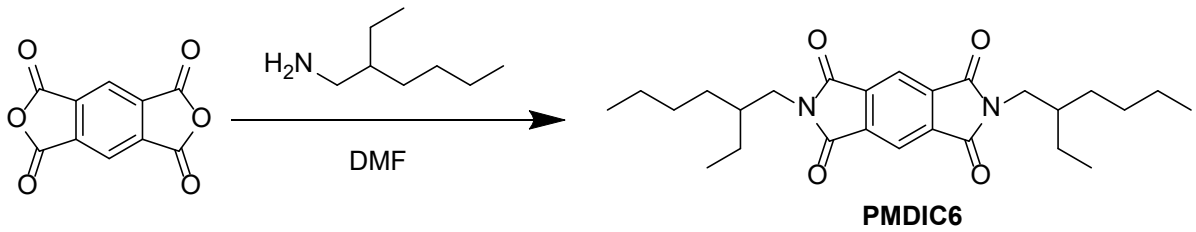


^{1}H NMR spectrum (400 MHz, DMSO-d_6, TMS standard) of **PyC6**.



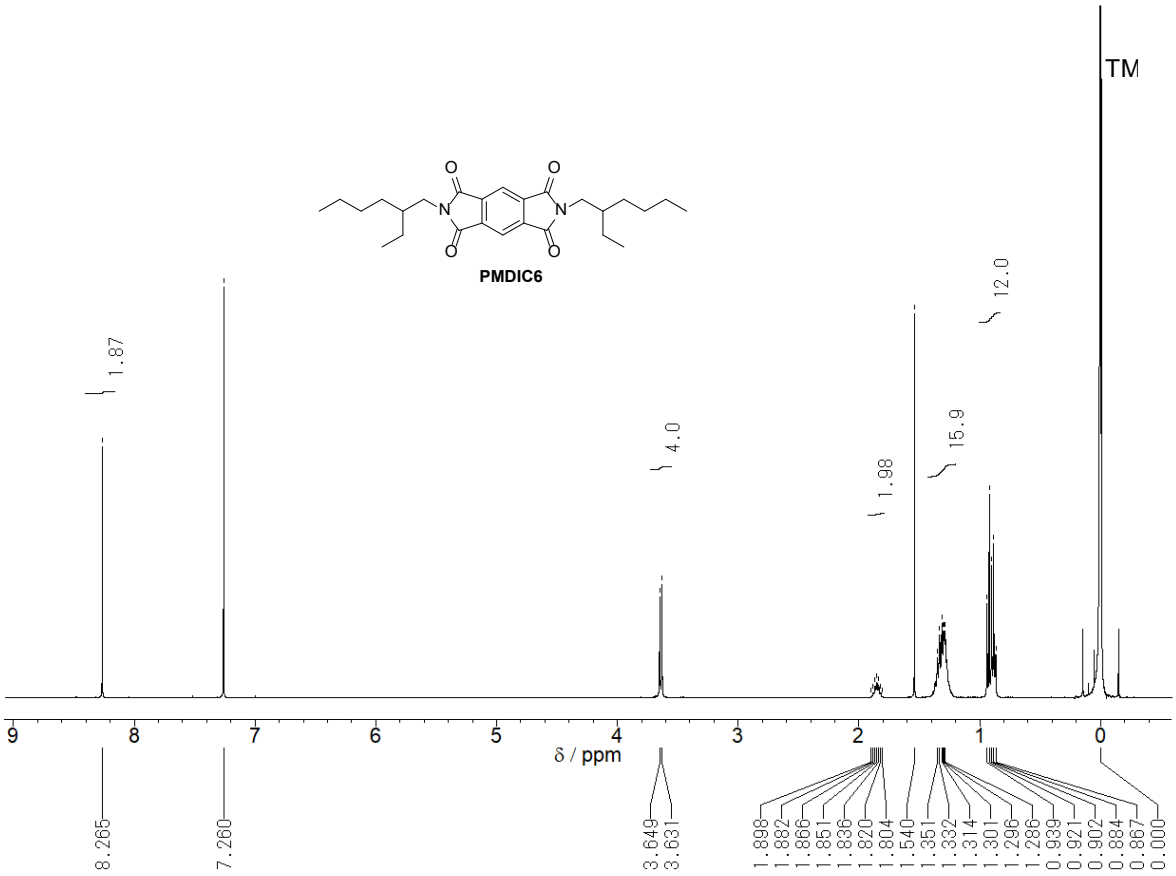
^{13}C NMR spectrum (100 MHz, DMSO-d_6, TMS standard) of **PyC6**.

Synthesis of **PMDIC6**[1]

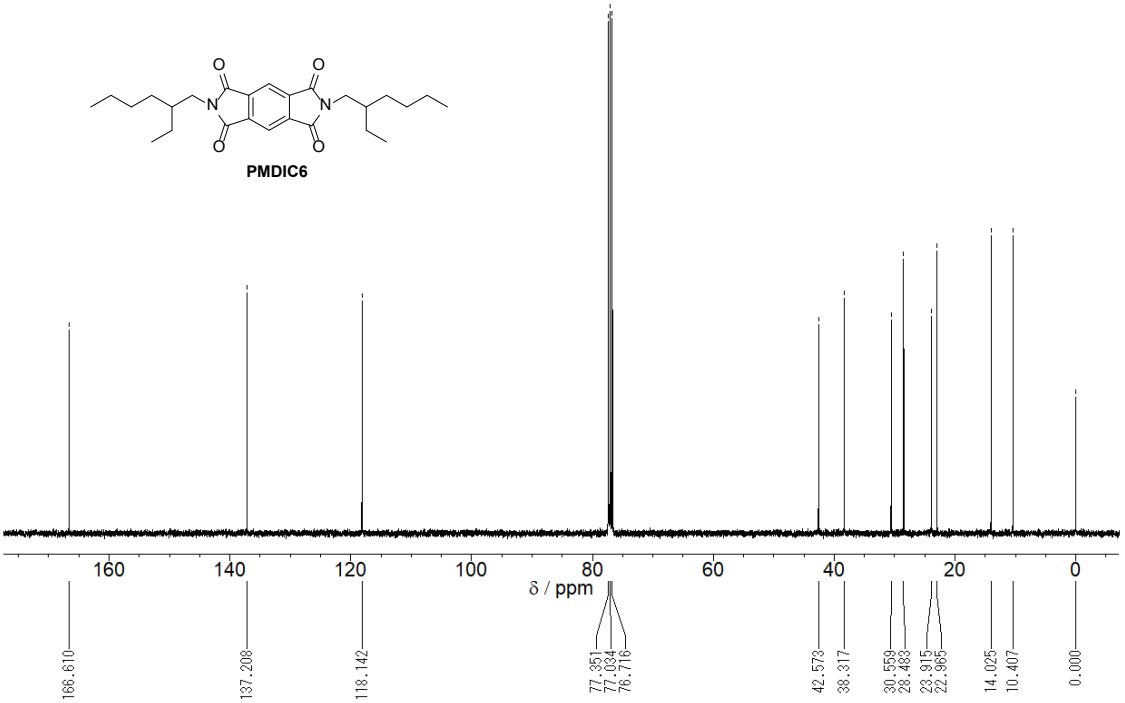


Under N_2, pyromellitic dianhydride (1.09 g, 5.0 mmol), and 2-ethylhexylamine (1.29 g, 10.0 mmol) in dry DMF (72 mL) were refluxed for 12 h. After cooling to the room temperature, the resulting mixture was poured into 1N HCl (250 mL) and then filtrated. The residue was dissolved in CH_2Cl_2 and dried over anhydrous $MgSO_4$, followed by evaporation to dryness. The residue was purified by silica gel column chromatography (CH_2Cl_2/Hexane=3/1) to obtain **PMDIC6** as a white solid (0.90 g, 2.0 mmol, 41%).

^{1}H NMR (400 MHz, $CDCl_3$, TMS standard): δ (ppm) 0.88 (t, *J* = 7.0 Hz, 6 H, C*H*$_3$), 0.92 (t, *J* = 7.4 Hz, 6 H, C*H*$_3$), 1.22-1.40 (m, 16 H, C*H*$_2$), 1.85 (sep, *J* = 6.3 Hz, 2 H, C*H*), 3.64 (d, *J* = 7.2 Hz, 4 H, C*H*$_2$), 8.27 (s, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$, TMS standard) δ (ppm) 10.41, 14.03, 22.97, 23.92, 28.48, 30.56, 38.32, 42.57, 118.14, 137.21, 166.61. HRMS(FAB) Calcd for $C_{26}H_{37}N_2O_4$ [$(M+H)^+$]: m/z 441.2753, Found: m/z 441.2764. Elemental analysis: calculated for $C_{26}H_{36}N_2O_4$: C 70.88, H 8.24, N 6.36, Found: C 70.72, H 7.99, N 6.45.

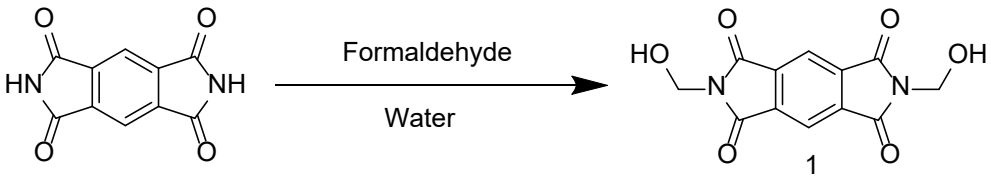


^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS standard) of **PMDIC6**.



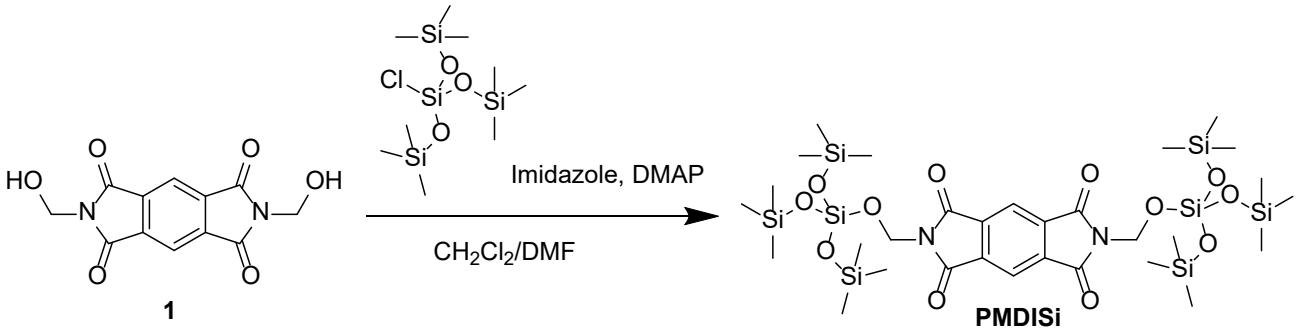
^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS standard) of **PMDIC6**.

Synthesis of **1**[2]



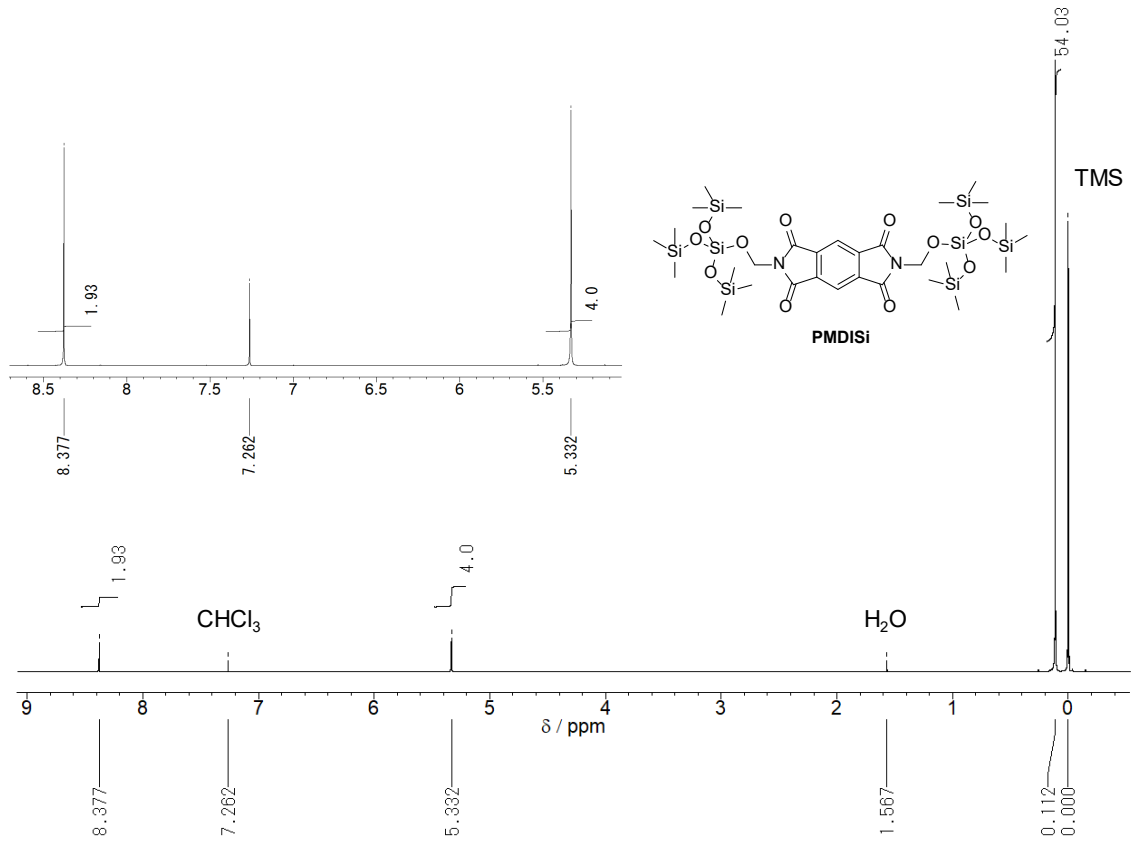
Pyromellitic Diimide (1.30 g, 6.0 mmol) and formaldehyde (37 wt%, 3.3 mL, 41 mmol) were suspended in 4 mL water and refluxed. After the reaction mixture was cooled to room temperature, it was filtrated and washed with water (200 mL). The residue was dried in vacuo, and suspended in hexane. The suspension was filtrated and washed with hexane (100 mL) and dried in vacuo to obtain compound **1** as white solid (1.28g, 4.6 mmol, 77%). ^{1}H NMR (400 MHz, DMSO-d_6, TMS standard): δ (ppm) 5.02 (d, J = 7.2 Hz, 4 H, CH_2), 6.56 (t, J = 7.0 Hz, 2 H, OH), 8.30 (s, 2 H, ArH); the ^{1}H NMR spectrum matches the literature data.[3]

Synthesis of **PMDISi**

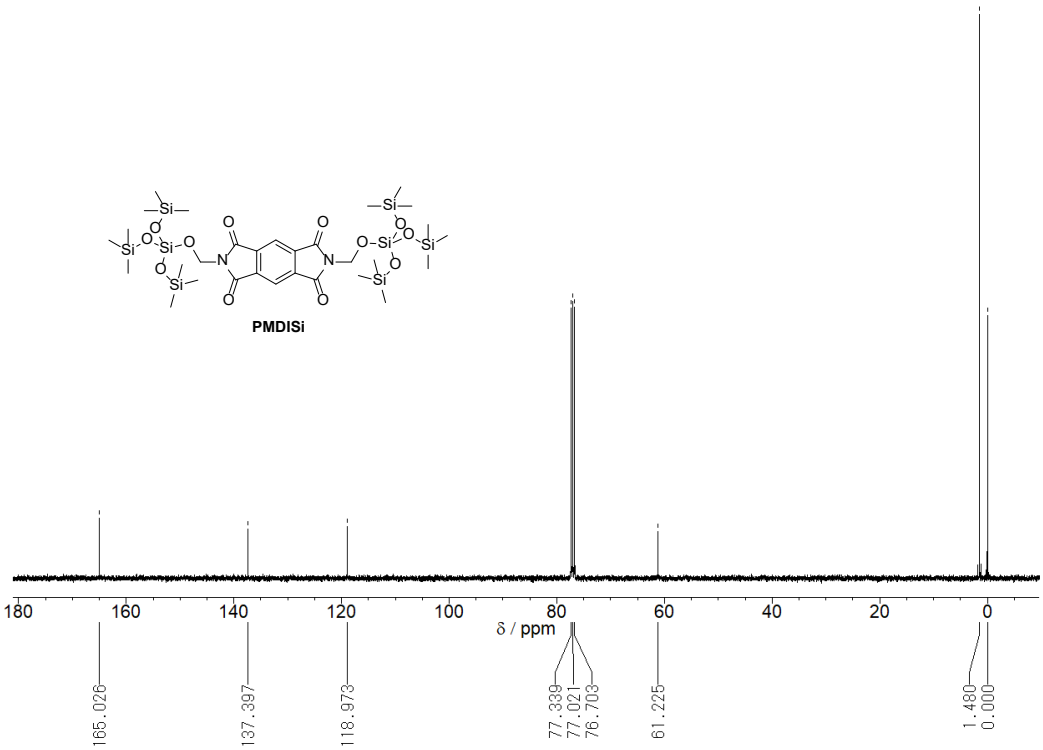


To a solution of **1** (1.10 g, 4.0 mmol), 4-dimethylaminopyridine (18 mg, 0.15 mmol) and imidazole (1.09 g, 16.0 mmol) in dry DMF (13 mL) and dry CH_2Cl_2 (32 mL), tris(trimethylsiloxy)chlorosilane (3.3 mL, 9.2 mmol) was slowly added at 0 °C under N_2. After the mixture was stirred for 2 h, it was poured into water and extracted with hexane/EtOAc (9/1). The organic layer was washed with water and dried over anhydrous Na_2SO_4, followed by evaporation to dryness. The residue was purified by column chromatography (Hexane/EtOAc=19/1 to 9/1) to obtain **PMDISi** as a white solid (1.45 g, 1.7 mmol, 42 %).

^{1}H NMR (400 MHz, $CDCl_3$, TMS standard): δ (ppm) 0.11 (s, 54 H, C*H*$_3$), 5.33 (s, 4 H, C*H*$_2$), 8.38 (s, 2 H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$, TMS standard): δ (ppm) 1.48, 61.22, 118.97, 137.40, 165.03. HRMS(FAB) Calcd for $C_{30}H_{61}N_2O_{12}Si_8$ [$(M+H)^+$]: m/z 865.2379, Found: m/z 865.2380.

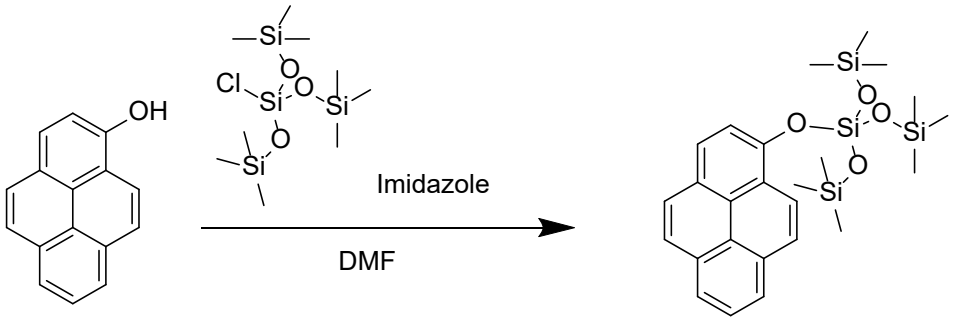


^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS standard) of **PMDISi**.



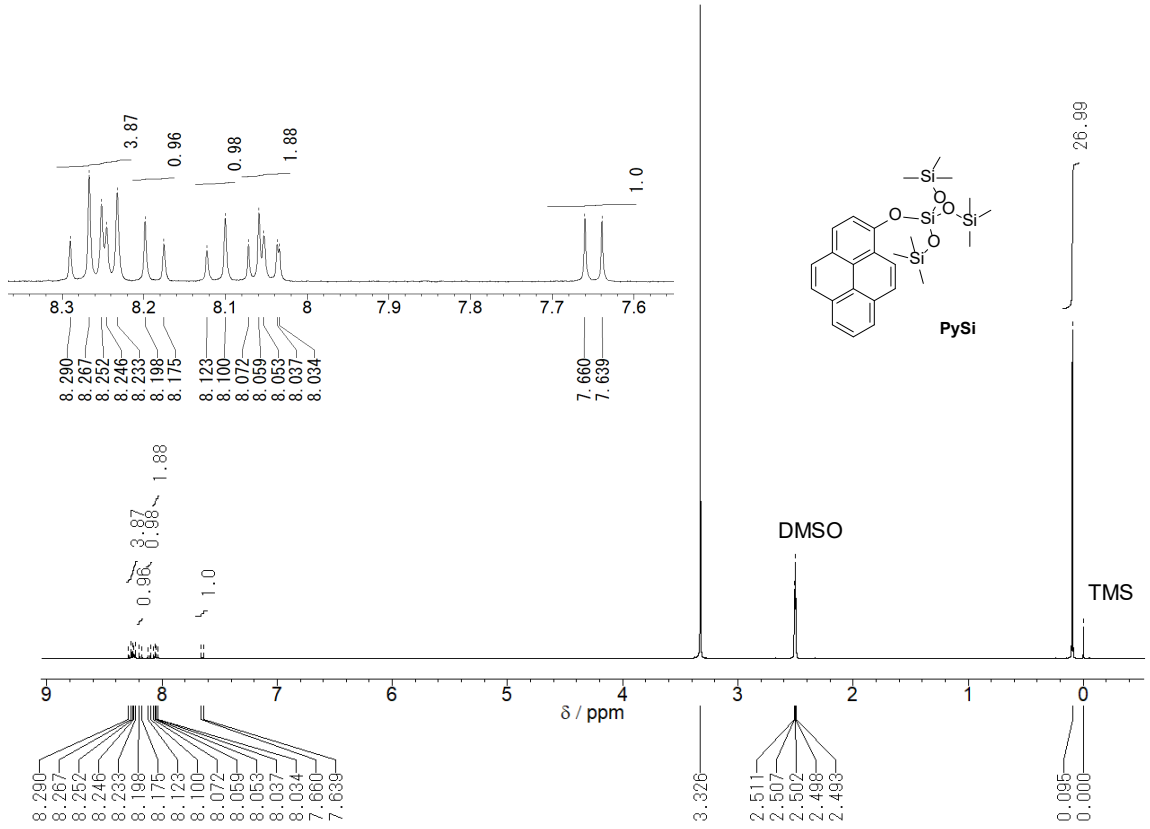
^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS standard) of **PMDISi**.

Synthesis of **PySi**

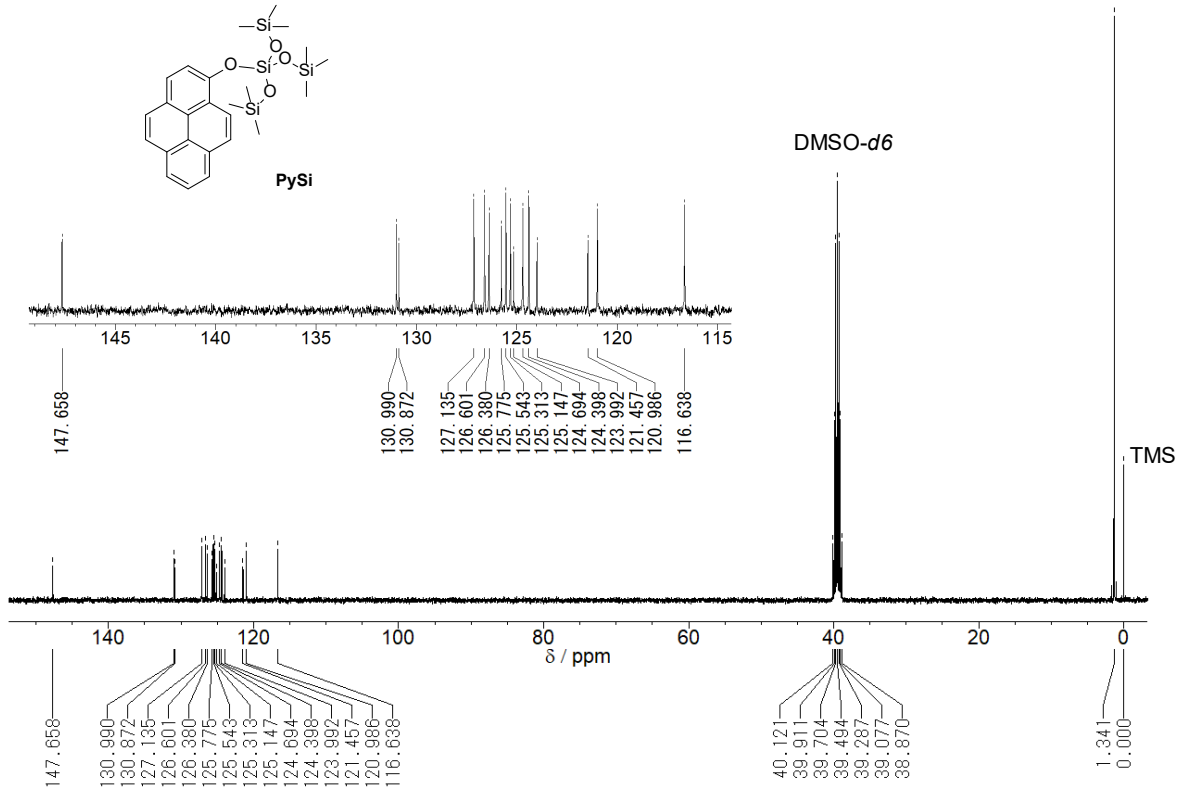


PySi

To a solution of 1-hydroxypyrene (2.50 g, 11.5 mmol) and imidazole (2.00 g, 29.5 mmol) in dry DMF (20 mL), tris(trimethylsiloxy)chlorosilane (6.5 mL, 18.1 mmol) was slowly added at 0 °C under N_2. After the mixture was stirred for 4 h, it was poured into water and extracted with hexane. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to give a yellow oil. The obtained oil was chromatographed (SiO_2, hexane:CH_2Cl_2 = 9:1) and then further chromatographed (SiO_2, hexane:EtOAc = 98:2) to obtain **PySi** as a white solid (4.41 g, 8.6 mmol, 75%). ^{1}H NMR (400 MHz, DMSO-d_6, TMS standard): δ (ppm) 0.10 (s, 27 H, CH_3), 7.65 (d, J = 8.4 Hz, 1 H, ArH), 8.02-8.08 (m, 2 H, ArH), 8.11 (d, J = 9.2 Hz, 1 H, ArH), 8.19 (d, J = 9.2 Hz, 1 H, ArH), 8.22-8.30 (m, 4 H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6, TMS standard): δ (ppm) 1.34, 116.64, 120.99, 121.46, 123.99, 124.40, 124.69, 125.15, 125.31, 125.54, 125.78, 126.38, 126.60, 127.14, 130.87, 130.99, 147.66. HRMS(FAB) Calcd for $C_{25}H_{37}O_4Si_4$ [$(M+H)^+$]: m/z 513.1769, Found: m/z 513.1765. Elemental analysis; calculated for $C_{25}H_{36}O_4Si_4$: C 58.54, H 7.08, Found: C 58.33, H 7.03.



^{1}H NMR spectrum (400 MHz, DMSO-d_6, TMS standard) of **PySi**.



^{13}C NMR spectrum (100 MHz, DMSO-d_6, TMS standard) of **PySi**.

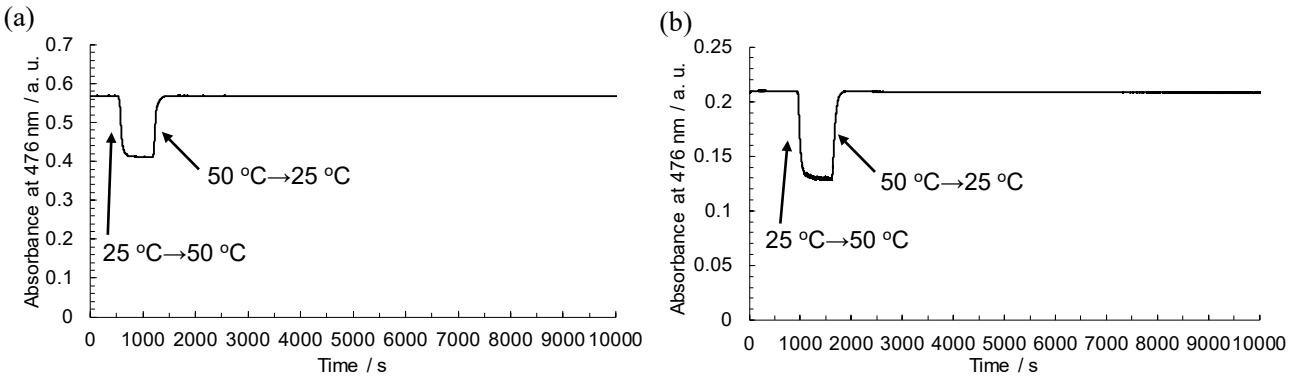


Fig. S1 Time dependence of the charge-transfer absorption of **PMDIC6-PyC6** in (a) PDMS(28000) and (b) *n*-hexane with varying temperature.

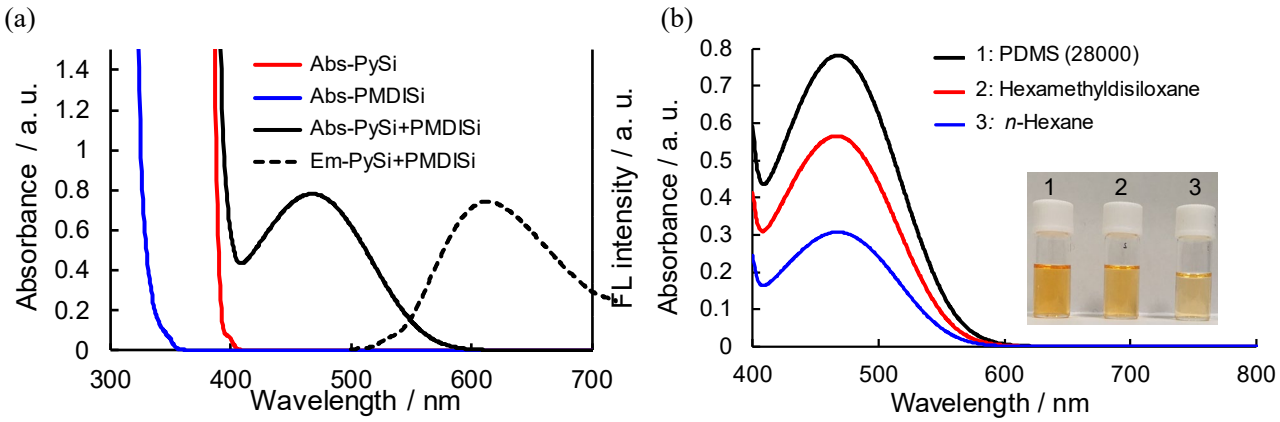


Fig. S2 (a) Absorption spectra of **PySi**, **PMDISi** and **PySi-PMDISi** and emission spectrum (λ_{ex} = 460 nm) of **PySi-PMDISi** in PDMS(28000) ([**PySi**] = 11 mM, [**PMDISi**] = 3 mM). (b) Absorption spectra and photographs of **PyC6-PMDISi** in PDMS(28000), hexamethyldisiloxane, *n*-hexane ([**PySi**]=11 mM, [**PMDISi**]=3 mM, 25 °C).

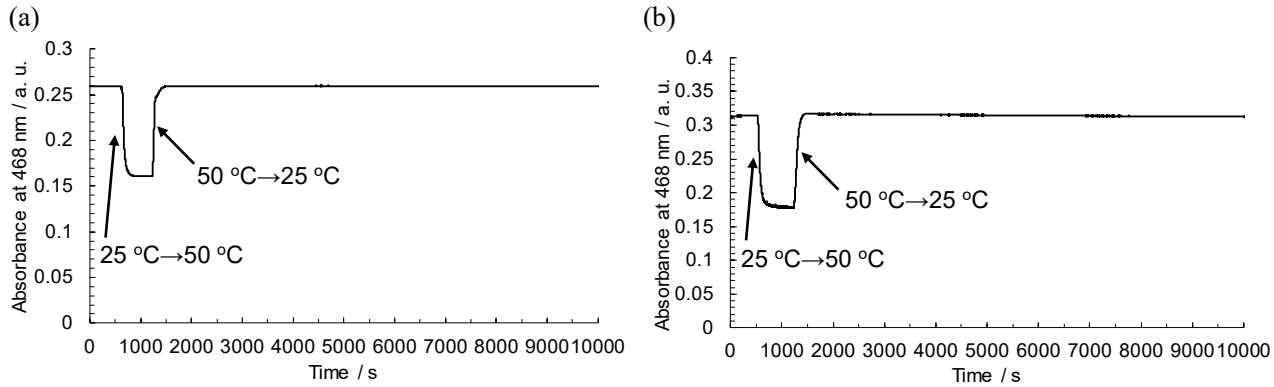


Fig. S3. Time dependence of the charge-transfer absorption of **PMDISi-PySi** in (a) PDMS(28000) and (b) *n*-hexane with varying temperature.

Evaluation of the association constant

The association constant (K_a) for **PMDIC6-PyC6**, **PMDISi-PySi**, **PMDIC6-PySi** and **PMDISi-PyC6** pairs were determined by measuring the absorbance of charge transfer absorption at different concentration of the solute. All measurements were carried out at 25 °C using cuvette with 1 cm path length. The association constants were evaluated by using non-linear curve fitting of the absorbance based on the equation S1 derived from a 1:1 binding model.

$$\mathrm{Abs} = \frac{\varepsilon l\left\{[\mathrm{A}]_0 + [\mathrm{D}]_0 + \frac{1}{K_a} - \sqrt{([\mathrm{A}]_0 + [\mathrm{D}]_0 + \frac{1}{K_a})^2 - 4[\mathrm{A}]_0[\mathrm{D}]_0}\right\}}{2} \qquad \text{(eqn S1)}$$

where $[\mathrm{D}]_0$, $[\mathrm{A}]_0$, $\boldsymbol{\varepsilon}$ and l are initial concentration of donor and acceptor molecules, molar absorption coefficient and optical path length respectively. To avoid an influence of 1:2 complex, the fittings were performed at low concentration of the donors at which saturation fractions were less than 0.55.

The sample for evaluation of the association constant were prepared by a dilution of the initial solution containing the acceptor and the donor with additional donor solution, in which the initial concentration of the donor was a large excess over the concentration of acceptor. The appropriate initial concentration of the donor was selected depending on the association constants of the solvent systems. All measurements were carried out after allowing the samples to stand at 25 °C for more than 5min.

Association constant for **PMDIC6-PyC6** in *n*-hexane

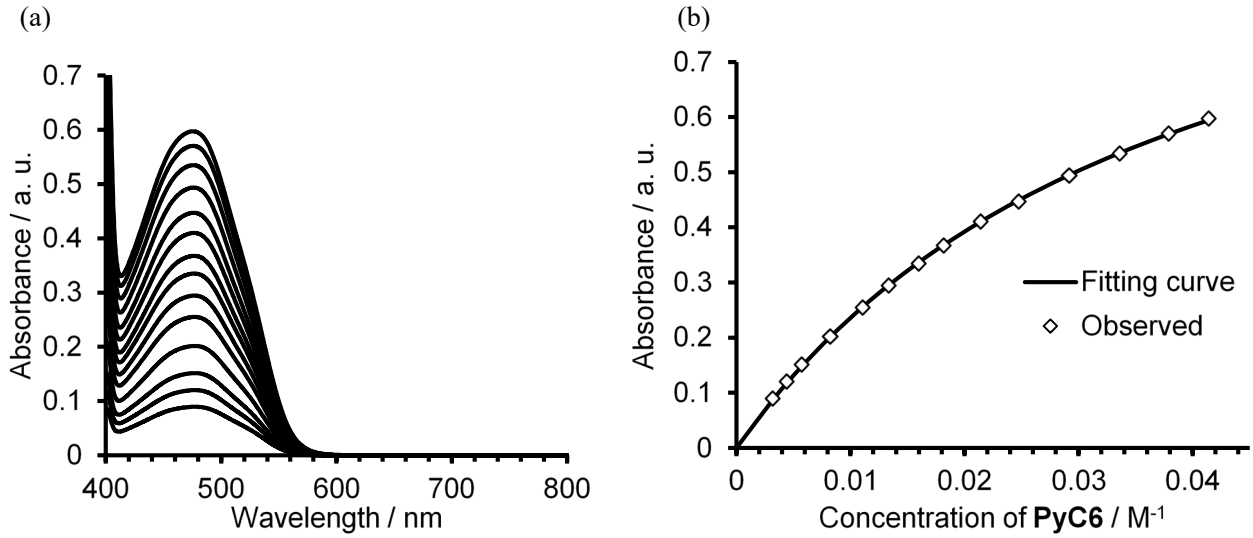


Fig. S4 (a) Absorption spectral variation of **PMDIC6-PyC6** system in *n*-hexane depending on concentration of **PyC6**. A solution containing 45.68 mM of **PyC6** and 2.50 mM of **PMDIC6** in *n*-hexane was diluted with 2.50 mM of **PMDIC6** in *n*-hexane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in 1-hexene

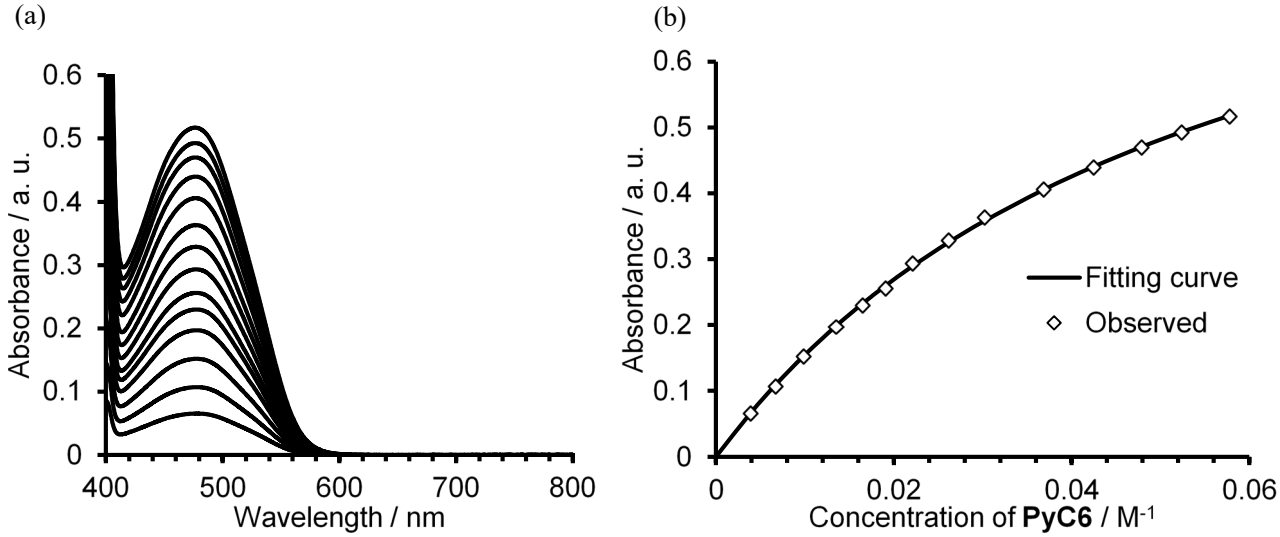


Fig. S5 (a) Absorption spectral variation of **PMDIC6-PyC6** system in 1-hexene depending on concentration of **PyC6**. A solution containing 57.78 mM of **PyC6** and 2.21 mM of **PMDIC6** in 1-hexene was diluted with 2.21 mM of **PMDIC6** in 1-hexene. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in tetrachloromethane

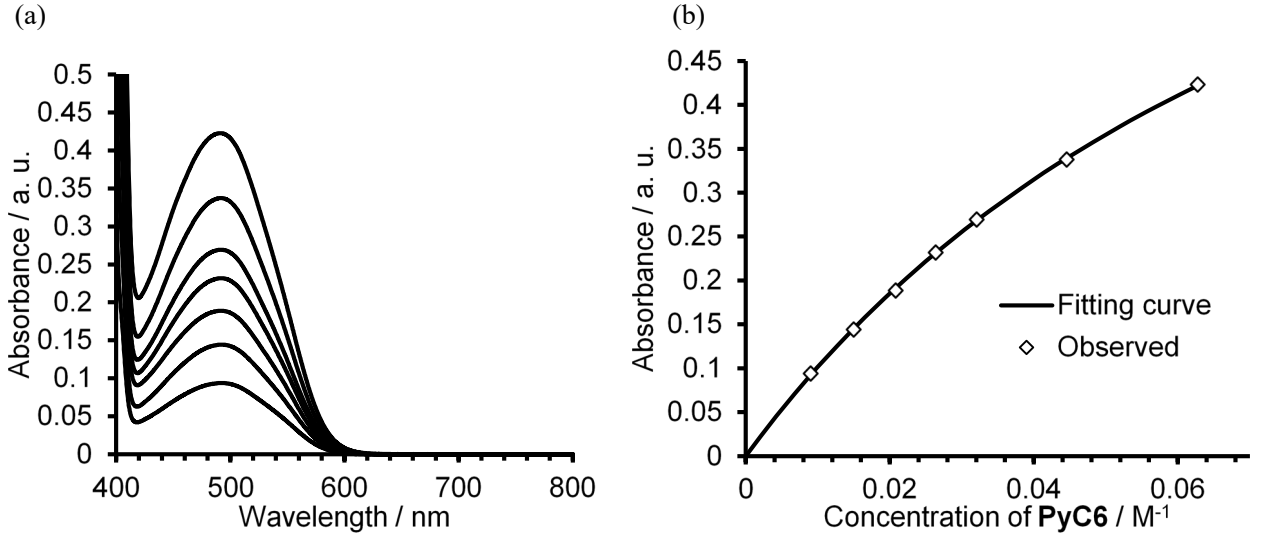


Fig. S6 (a) Absorption spectral variation of **PMDIC6-PyC6** system in tetrachloromethane depending on concentration of **PyC6**. A solution containing 62.77 mM of **PyC6** and 2.30 mM of **PMDIC6** in tetrachloromethane was diluted with 2.30 mM of **PMDIC6** in tetrachloromethane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in di-*n*-butyl ether

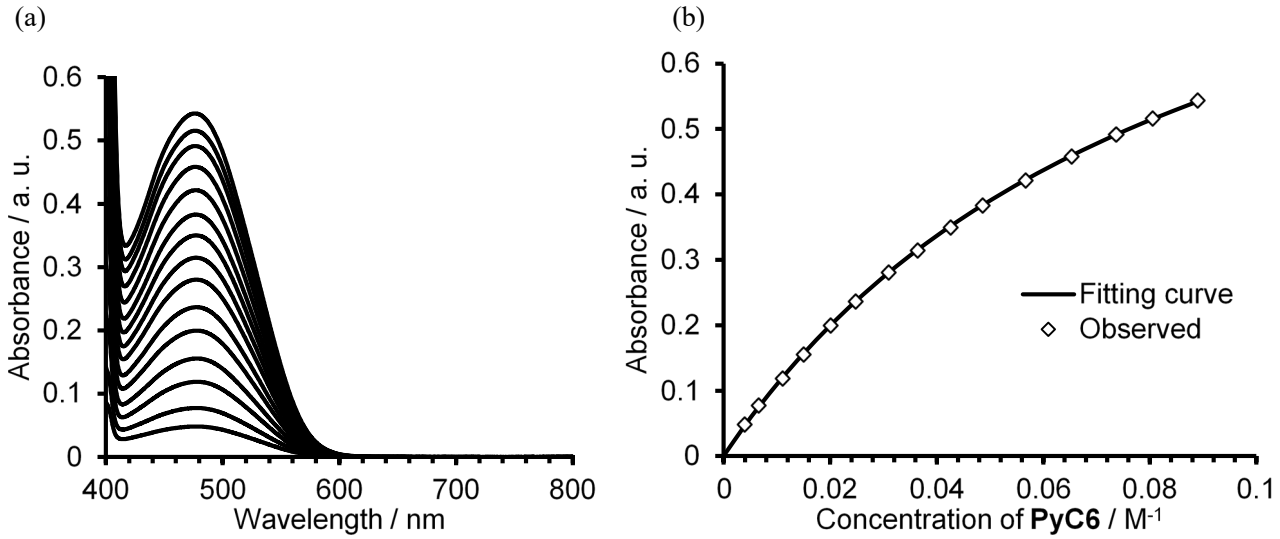


Fig. S7 (a) Absorption spectral variation of **PMDIC6-PyC6** system in di-*n*-butyl ether depending on concentration of **PyC6**. A solution containing 88.87 mM of **PyC6** and 2.31 mM of **PMDIC6** in di-*n*-butyl ether was diluted with 2.31 mM of **PMDIC6** in di-*n*-butyl ether. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in *tert*-butyl methyl ether

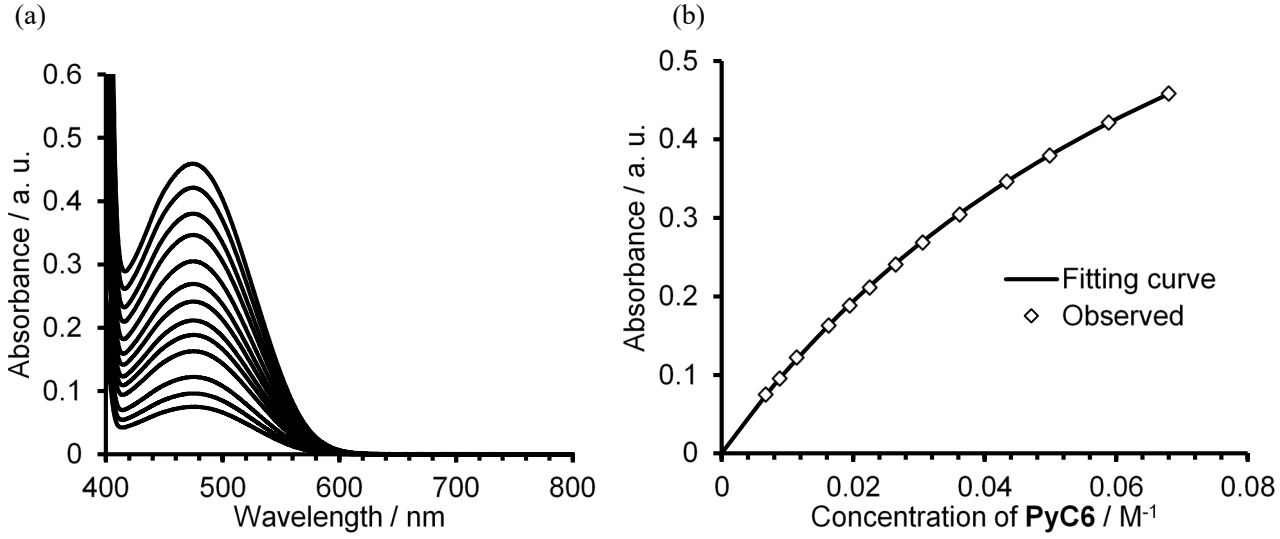


Fig. S8 (a) Absorption spectral variation of **PMDIC6-PyC6** system in *tert*-butyl methyl ether depending on concentration of **PyC6**. A solution containing 67.93 mM of **PyC6** and 2.63 mM of **PMDIC6** in *tert*-butyl methyl ether was diluted with 2.63 mM of **PMDIC6** in *tert*-butyl methyl ether. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in diethyldiglycol

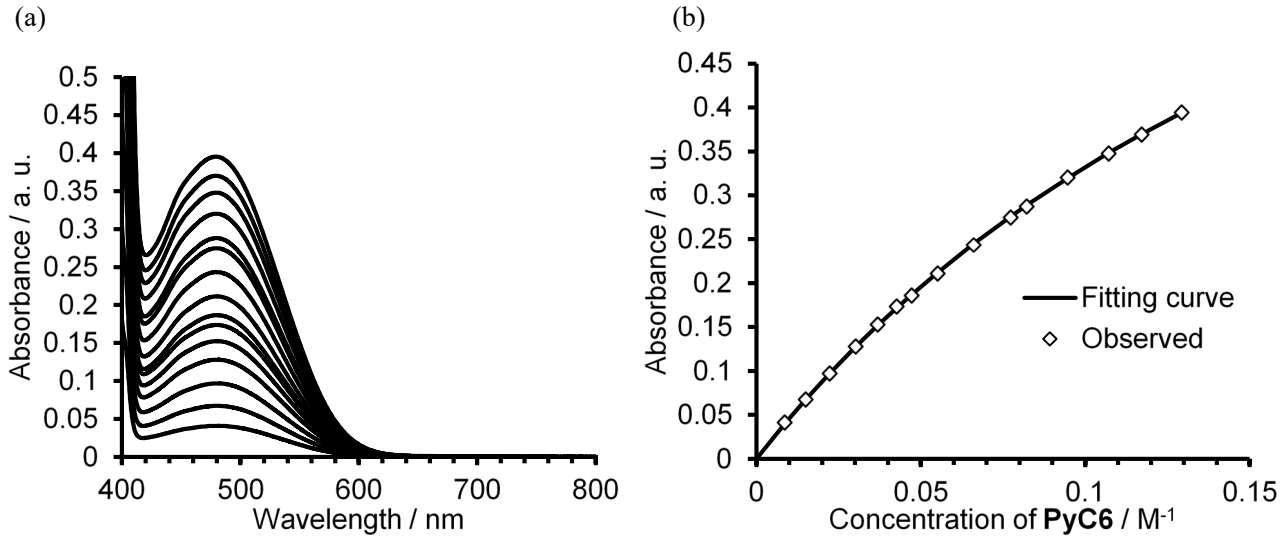


Fig. S9 (a) Absorption spectral variation of **PMDIC6-PyC6** system in diethyldiglycol depending on concentration of **PyC6**. A solution containing 129.3 mM of **PyC6** and 2.30 mM of **PMDIC6** in diethyldiglycol ether was diluted with 2.30 mM of **PMDIC6** in diethyldiglycol. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in chloroform

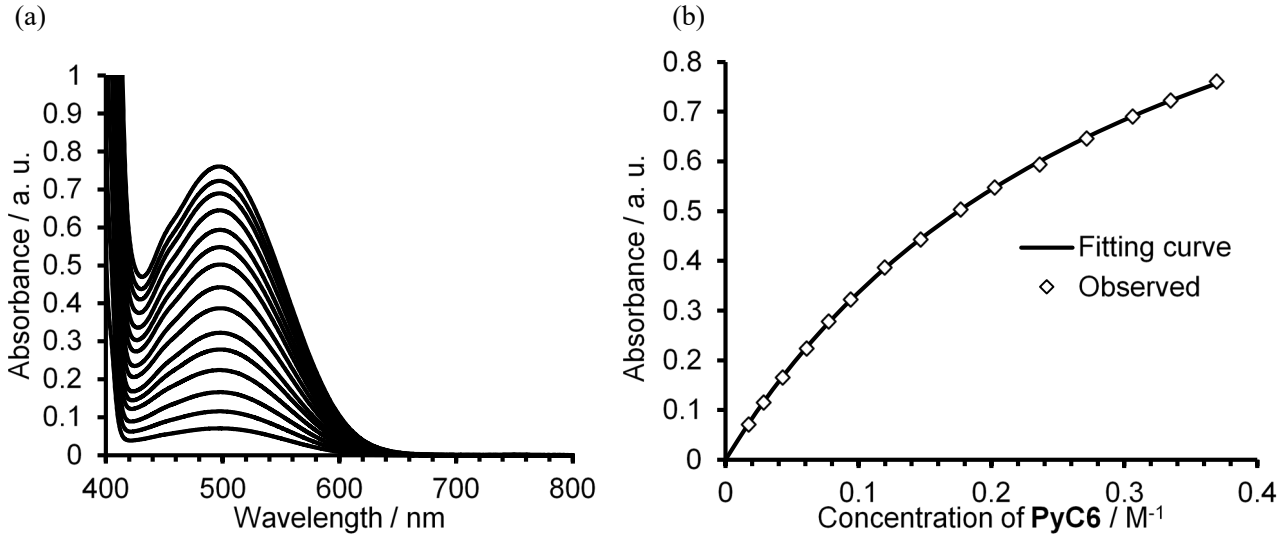


Fig. S10 (a) Absorption spectral variation of **PMDIC6-PyC6** system in chloroform depending on concentration of **PyC6**. A solution containing 369.50 mM of **PyC6** and 2.74 mM of **PMDIC6** in chloroform was diluted with 2.74 mM of **PMDIC6** in chloroform. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in acetone

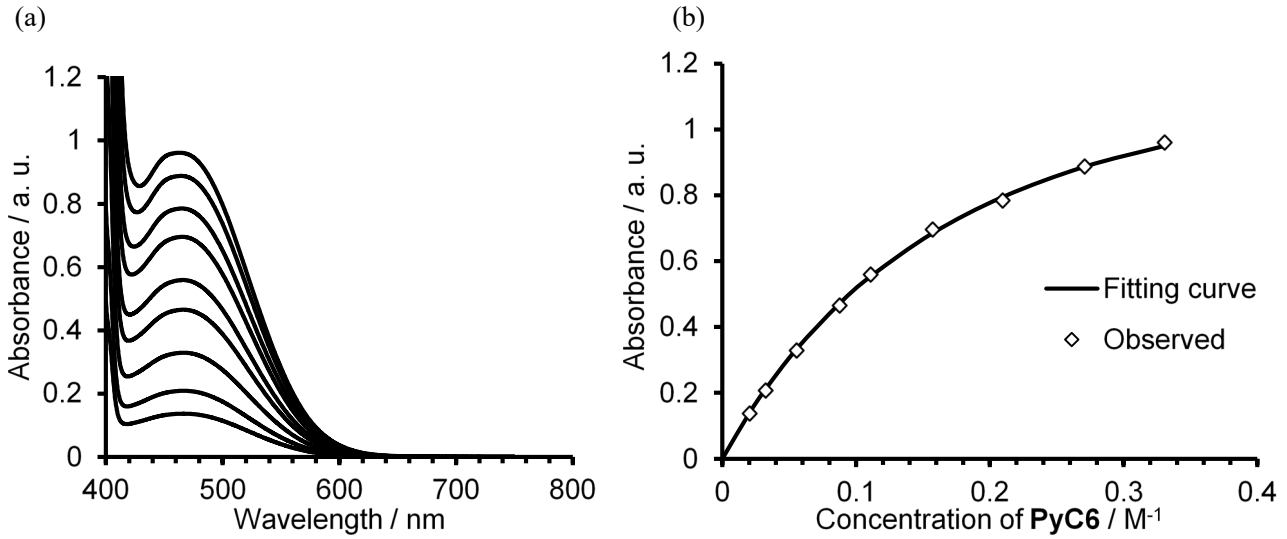


Fig. S11 (a) Absorption spectral variation of **PMDIC6-PyC6** system in acetone depending on concentration of **PyC6**. A solution containing 381.76 mM of **PyC6** and 3.33 mM of **PMDIC6** in acetone was diluted with 3.80 mM of **PMDIC6** in acetone. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in DMSO

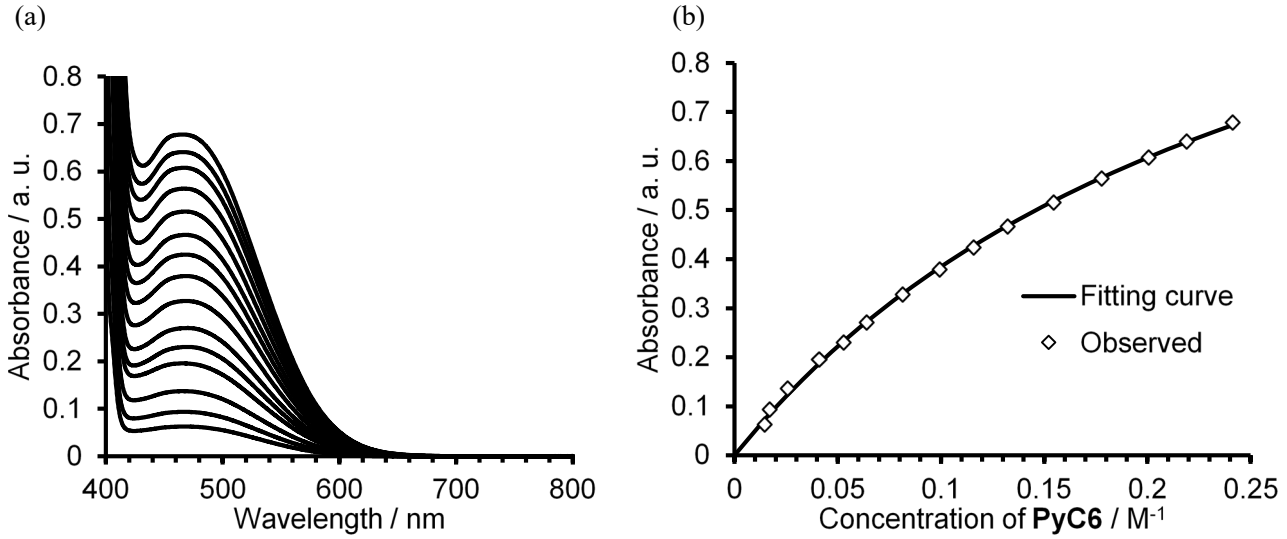


Fig. S12 (a) Absorption spectral variation of **PMDIC6-PyC6** system in DMSO depending on concentration of **PyC6**. A solution containing 241.35 mM of **PyC6** and 2.64 mM of **PMDIC6** in DMSO was diluted with 2.64 mM of **PMDIC6** in DMSO. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in acetonitrile

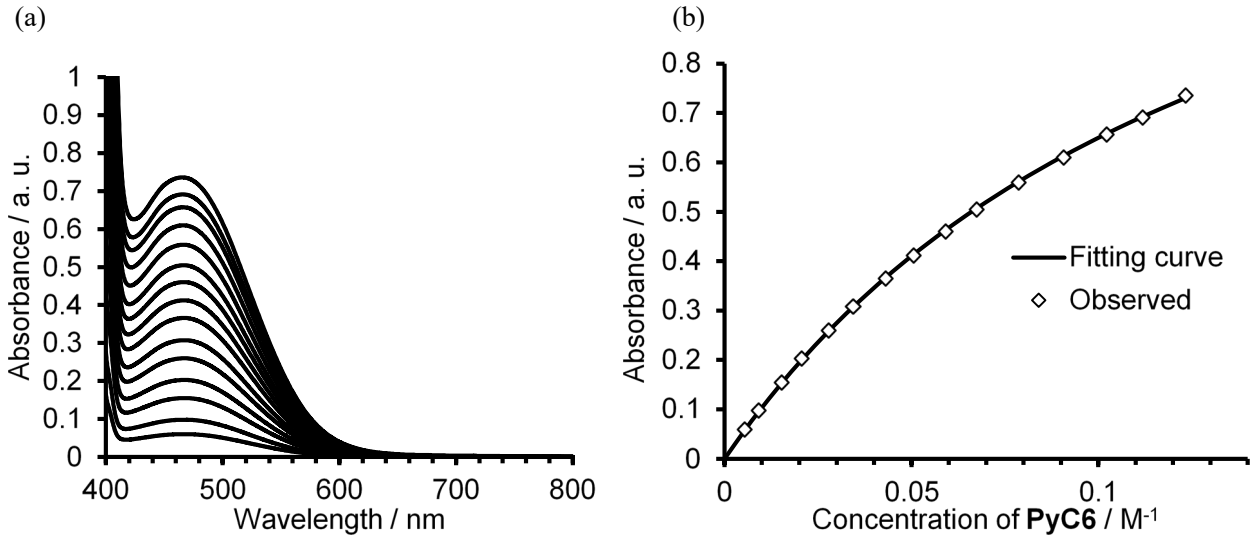


Fig. S13 (a) Absorption spectral variation of **PMDIC6-PyC6** system in acetonitrile depending on concentration of **PyC6**. A solution containing 123.25 mM of **PyC6** and 3.10 mM of **PMDIC6** in acetonitrile was diluted with 3.10 mM of **PMDIC6** in acetonitrile. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in ethanol

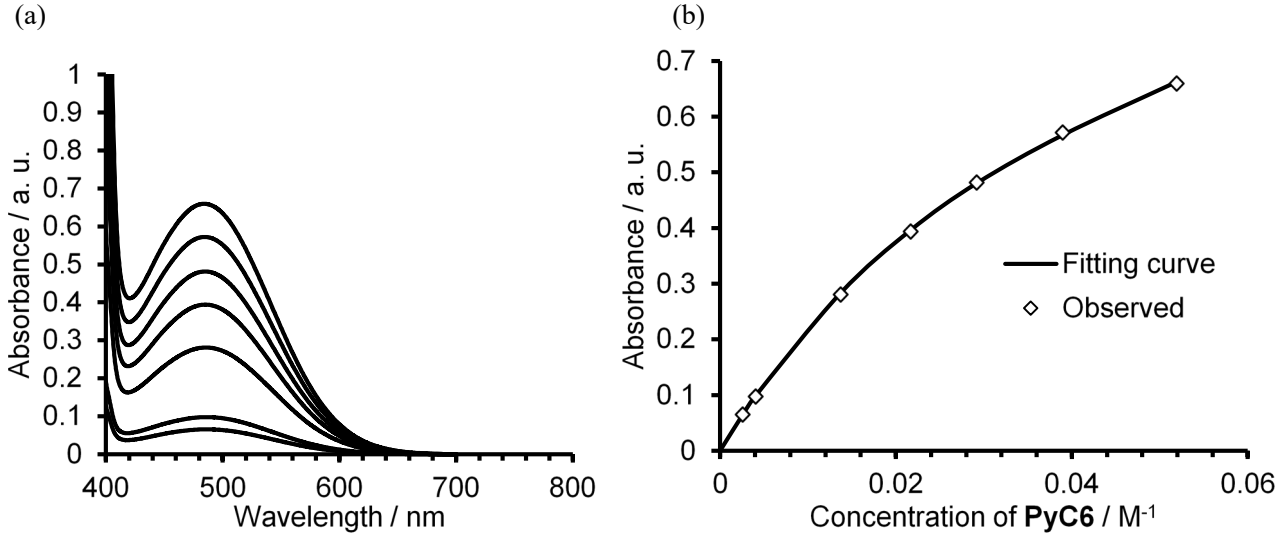


Fig. S14 (a) Absorption spectral variation of **PMDIC6-PyC6** system in ethanol depending on concentration of **PyC6**. A solution containing 95.17 mM of **PyC6** and 2.67 mM of **PMDIC6** in ethanol was diluted with 2.76 mM of **PMDIC6** in ethanol. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in methanol

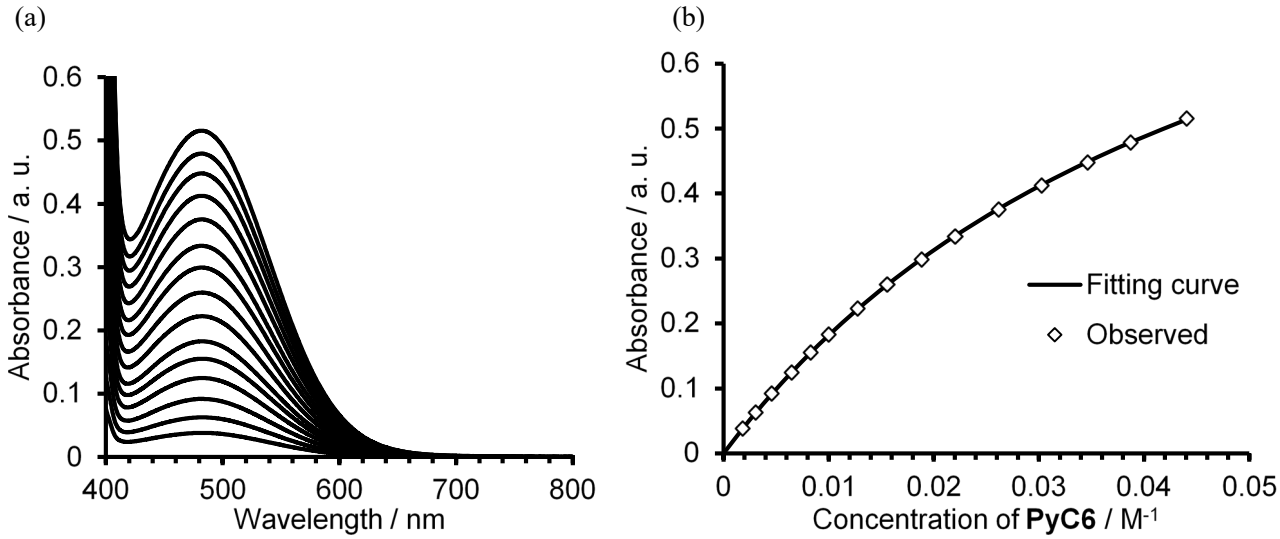


Fig. S15 (a) Absorption spectral variation of **PMDIC6-PyC6** system in methanol depending on concentration of **PyC6**. A solution containing 44.03 mM of **PyC6** and 2.32 mM of **PMDIC6** in methanol was diluted with 2.32 mM of **PMDIC6** in methanol. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in hexamethyldisiloxane

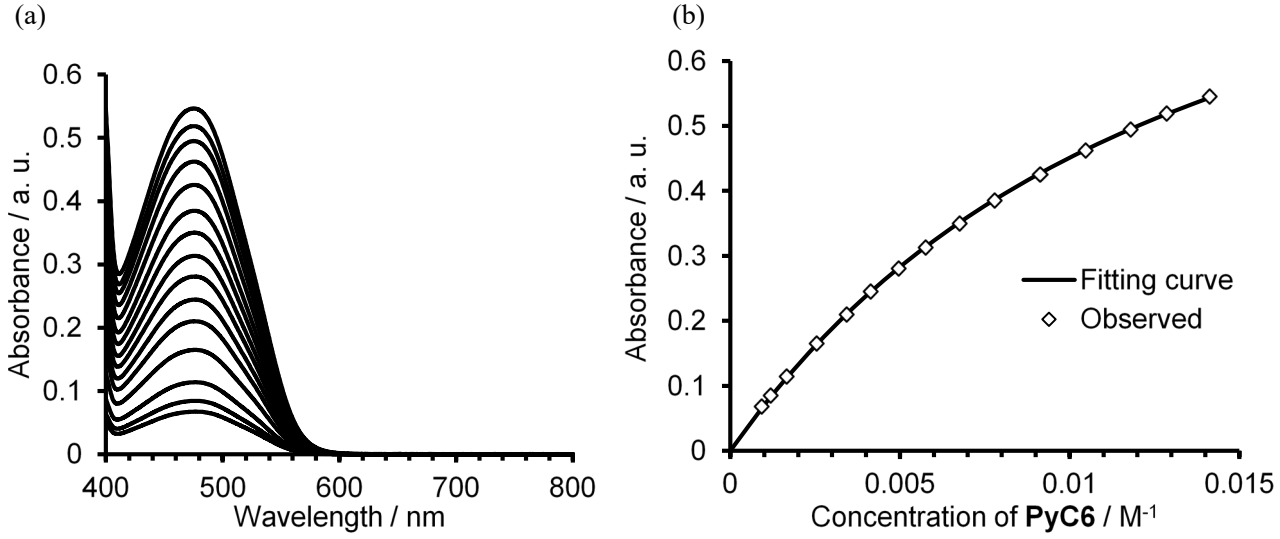


Fig. S16 (a) Absorption spectral variation of **PMDIC6-PyC6** system in hexamethyldisiloxane depending on concentration of **PyC6**. A solution containing 14.14 mM of **PyC6** and 2.38 mM of **PMDIC6** in hexamethyldisiloxane was diluted with 2.38 mM of **PMDIC6** in hexamethyldisiloxane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in octamethyltrisiloxane

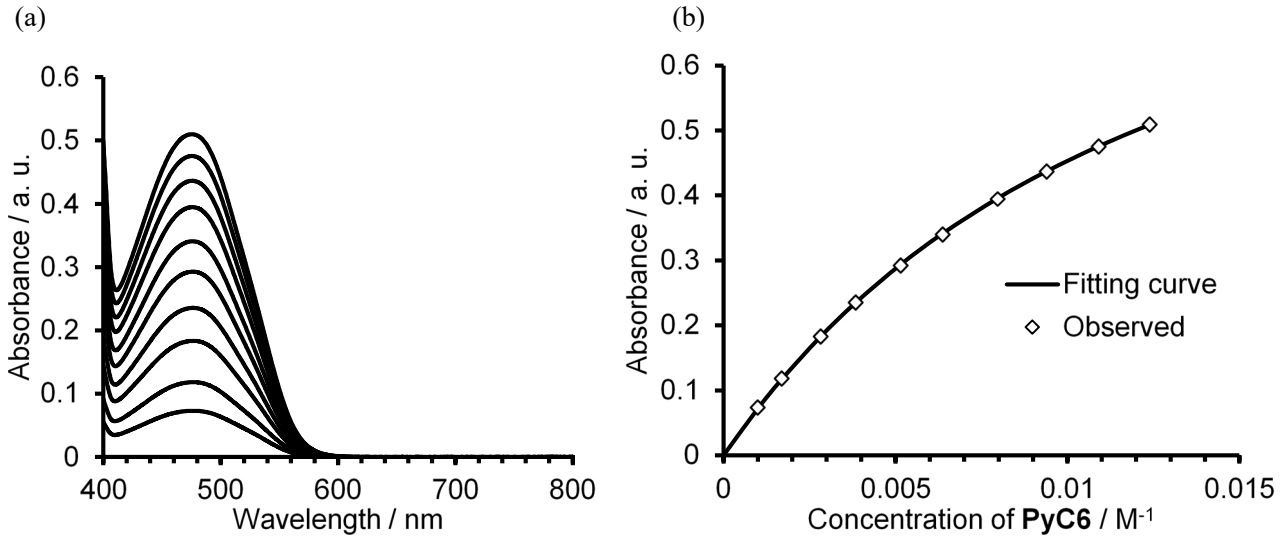


Fig. S17 (a) Absorption spectral variation of **PMDIC6-PyC6** system in octamethyltrisiloxane depending on concentration of **PyC6**. A solution containing 22.68 mM of **PyC6** and 2.31 mM of **PMDIC6** in octamethyltrisiloxane was diluted with 2.31 mM of **PMDIC6** in octamethyltrisiloxane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in decamethyltetrasiloxane

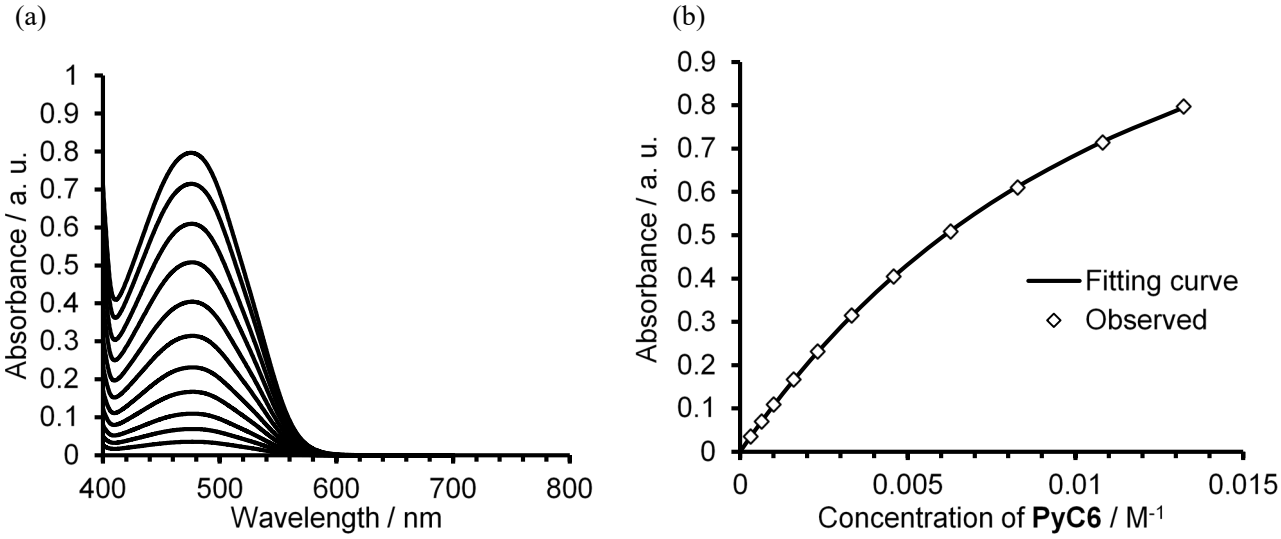


Fig. S18 (a) Absorption spectral variation of **PMDIC6-PyC6** system in decamethyltetrasiloxane depending on concentration of **PyC6**. A solution containing 13.21 mM of **PyC6** and 3.60 mM of **PMDIC6** in decamethyltetrasiloxane was diluted with 3.60 mM of **PMDIC6** in decamethyltetrasiloxane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in dodecamethylpentasiloxane

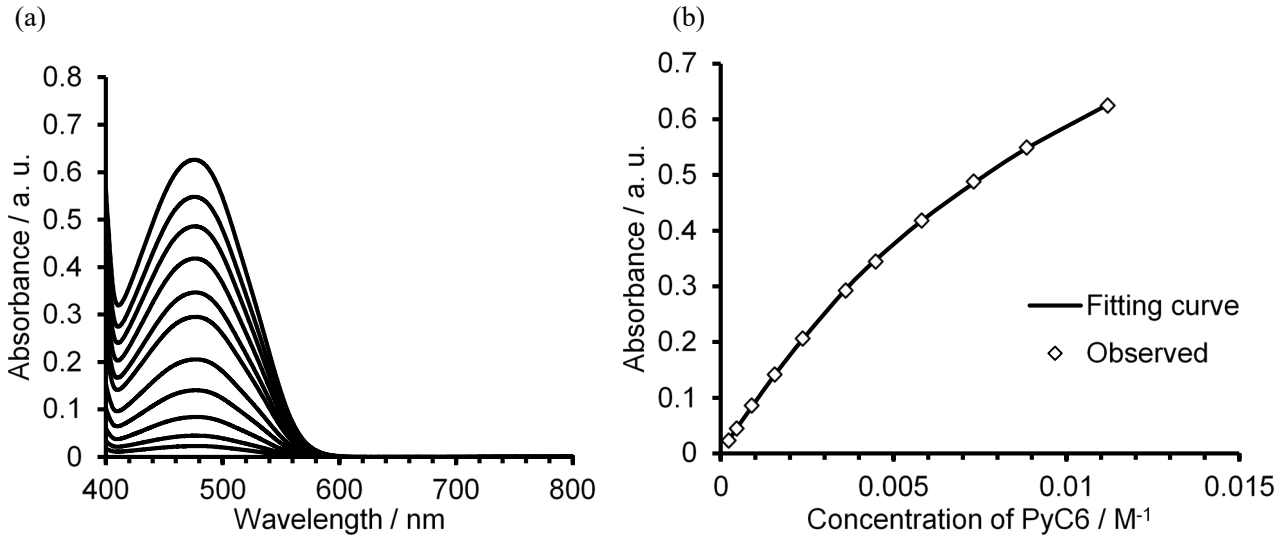


Fig. S19 (a) Absorption spectral variation of **PMDIC6-PyC6** system in dodecamethylpentasiloxane depending on concentration of **PyC6**. A solution containing 11.18 mM of **PyC6** and 2.92 mM of **PMDIC6** in dodecamethylpentasiloxane was diluted with 2.92 mM of **PMDIC6** in dodecamethylpentasiloxane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in PDMS(2000)

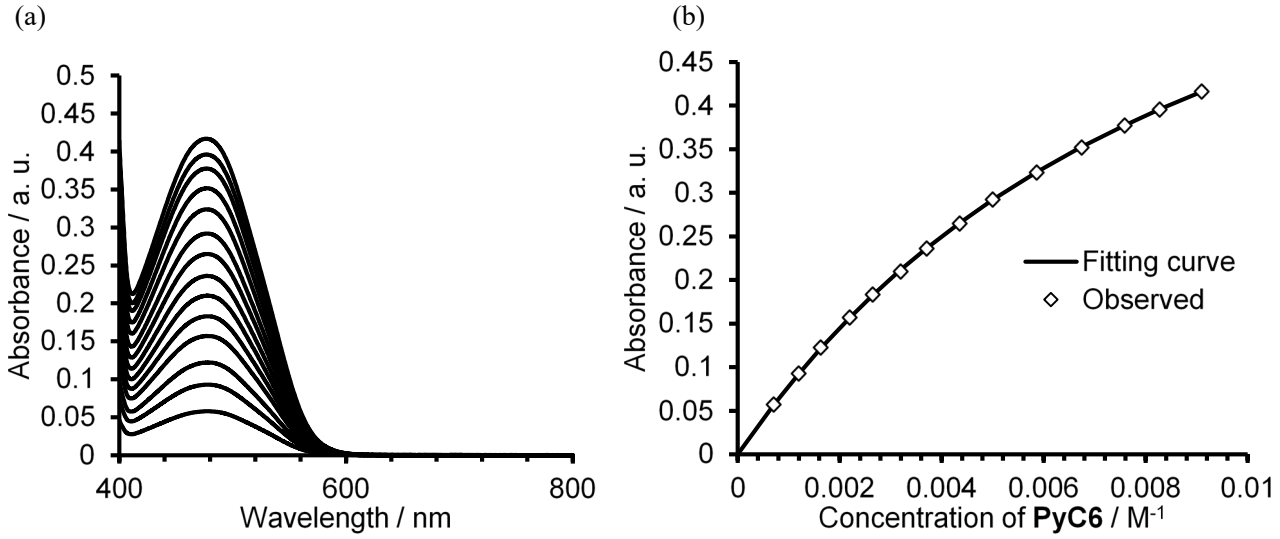


Fig. S20 (a) Absorption spectral variation of **PMDIC6-PyC6** system in PDMS(2000) depending on concentration of **PyC6**. A solution containing 9.09 mM of **PyC6** and 1.89 mM of **PMDIC6** in PDMS(2000) was diluted with 1.89 mM of **PMDIC6** in PDMS(2000). (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in PDMS(28000)

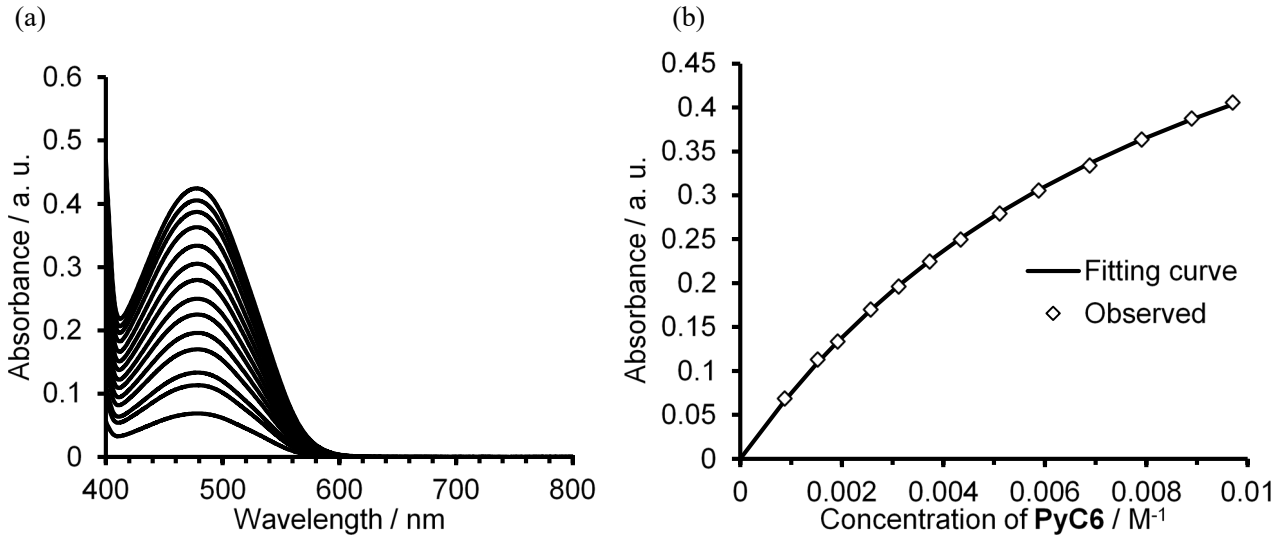


Fig. S21 (a) Absorption spectral variation of **PMDIC6-PyC6** system in PDMS(28000) depending on concentration of **PyC6**. A solution containing 10.66 mM of **PyC6** and 1.81 mM of **PMDIC6** in PDMS(28000) was diluted with 1.81 mM of **PMDIC6** in PDMS(28000). (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in 2,2,4,4,6,8,8-heptamethylnonane

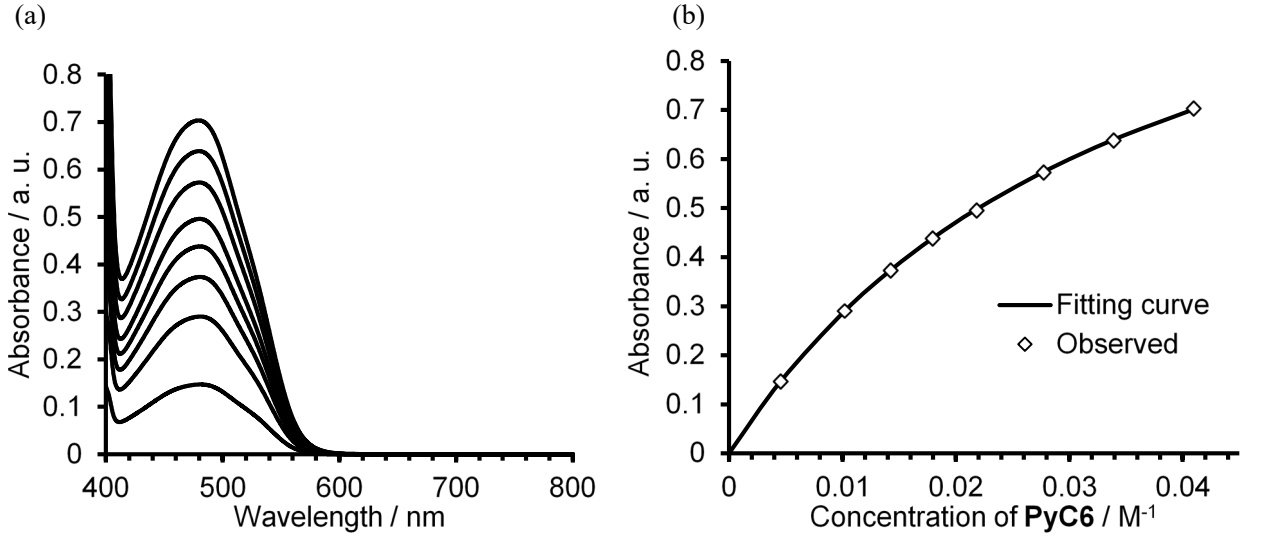


Fig. S22 (a) Absorption spectral variation of **PMDIC6-PyC6** system in 2,2,4,4,6,8,8-heptamethylnonane depending on concentration of **PyC6**. A solution containing 40.99 mM of **PyC6** and 2.72 mM of **PMDIC6** in 2,2,4,4,6,8,8-heptamethylnonane was diluted with 2.72 mM of **PMDIC6** in 2,2,4,4,6,8,8-heptamethylnonane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PyC6** in bis(trimethylsilyl)methane

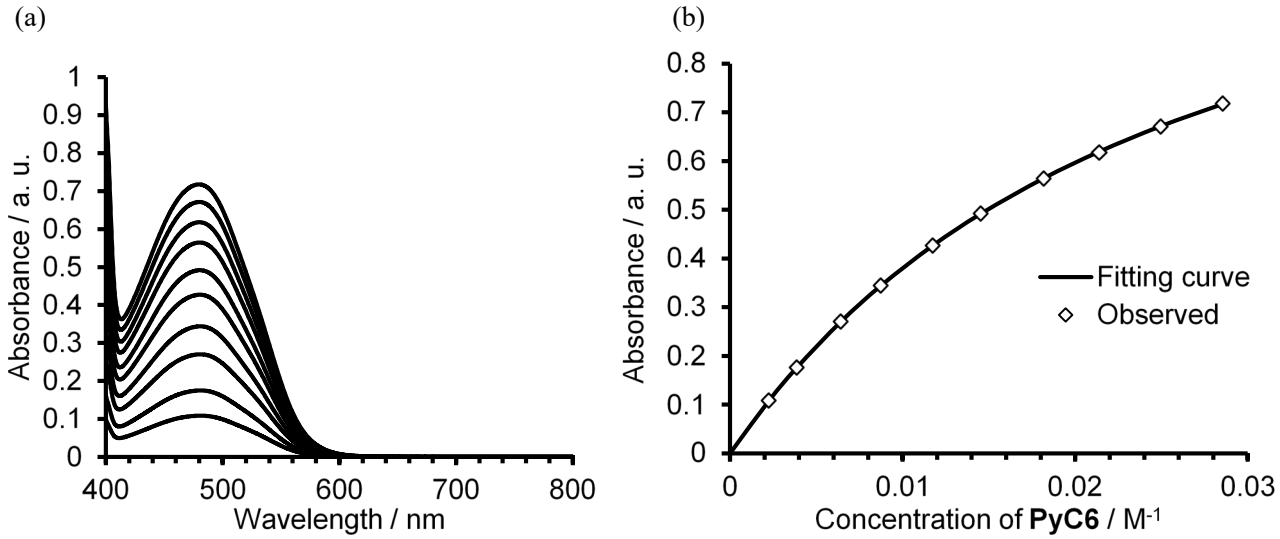


Fig. S23 (a) Absorption spectral variation of **PMDIC6-PyC6** system in bis(trimethylsilyl)methane depending on concentration of **PyC6**. A solution containing 28.51 mM of **PyC6** and 2.96 mM of **PMDIC6** in bis(trimethylsilyl)methane was diluted with 2.96 mM of **PMDIC6** in bis(trimethylsilyl)methane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDISi-PySi** in *n*-hexane

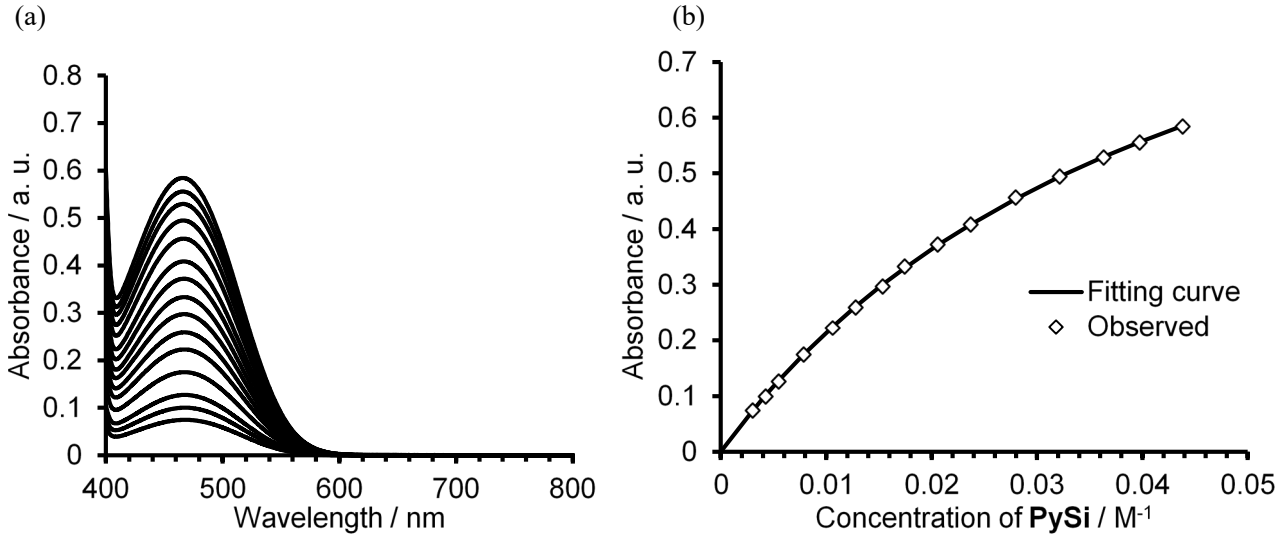


Fig. S24 (a) Absorption spectral variation of **PMDISi-PySi** system in *n*-hexane depending on concentration of **PySi**. A solution containing 43.79 mM of **PySi** and 2.33 mM of **PMDISi** in *n*-hexane was diluted with 2.33 mM of **PMDISi** in *n*-hexane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDISi-PySi** in hexamethyldisiloxane

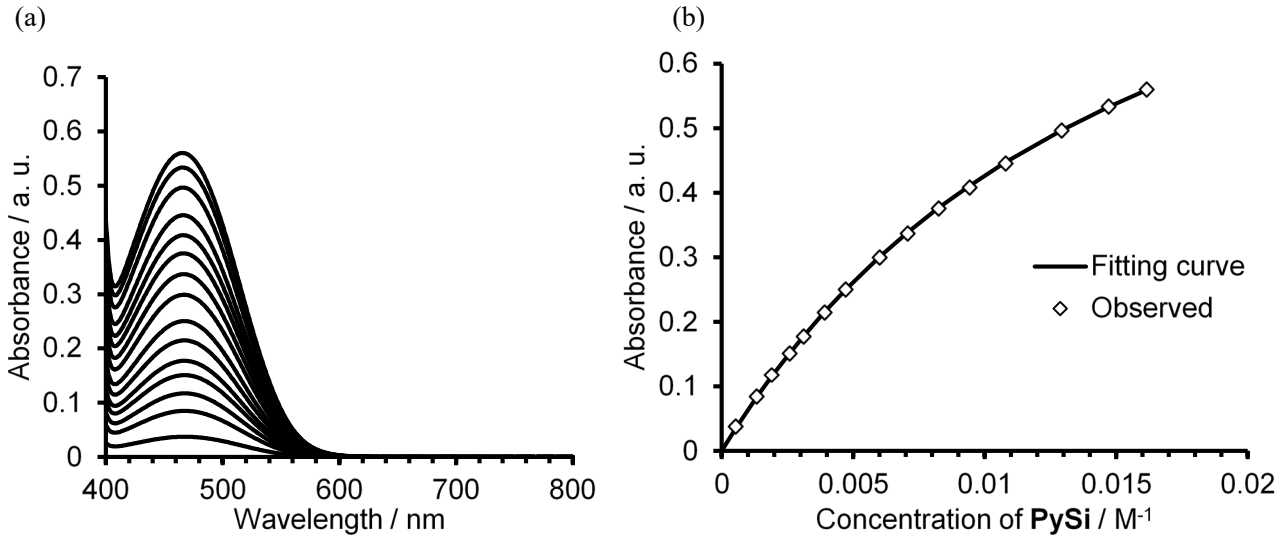


Fig. S25 (a) Absorption spectral variation of **PMDISi-PySi** system in hexamethyldisiloxane depending on concentration of **PySi**. A solution containing 17.96 mM of **PySi** and 2.31 mM of **PMDISi** in hexamethyldisiloxane was diluted with 2.31 mM of **PMDISi** in hexamethyldisiloxane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDISi-PySi** in octamethyltrisiloxane

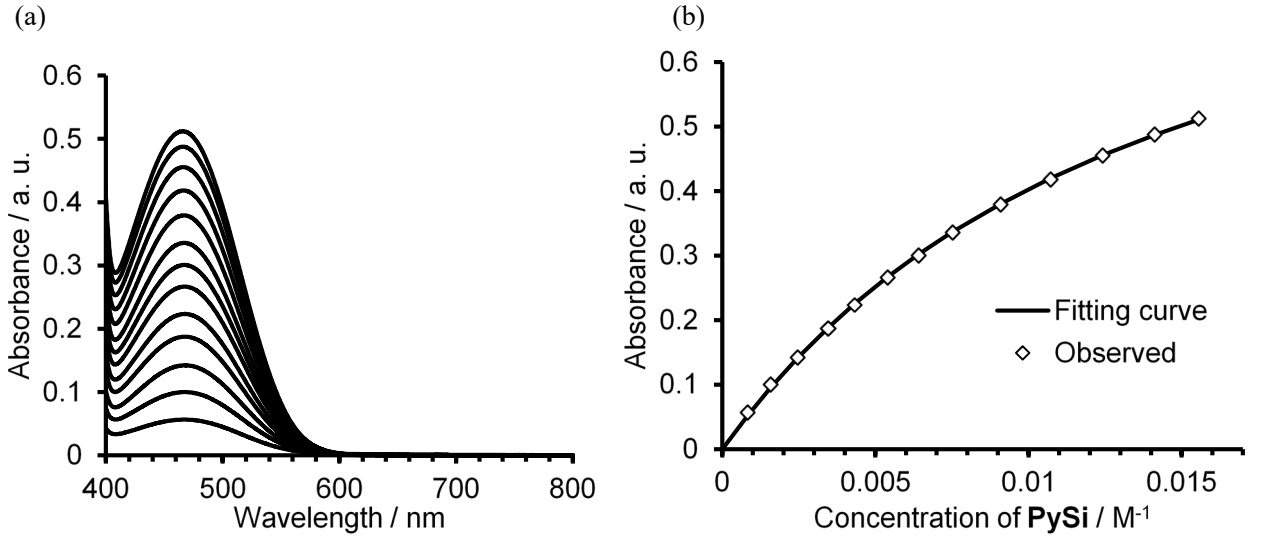


Fig. S26 (a) Absorption spectral variation of **PMDISi-PySi** system in octamethyltrisiloxane depending on concentration of **PySi**. A solution containing 15.54 mM of **PySi** and 1.99 mM of **PMDISi** in octamethyltrisiloxane was diluted with 1.99 mM of **PMDISi** in octamethyltrisiloxane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDISi-PySi** in decamethyltetrasiloxane

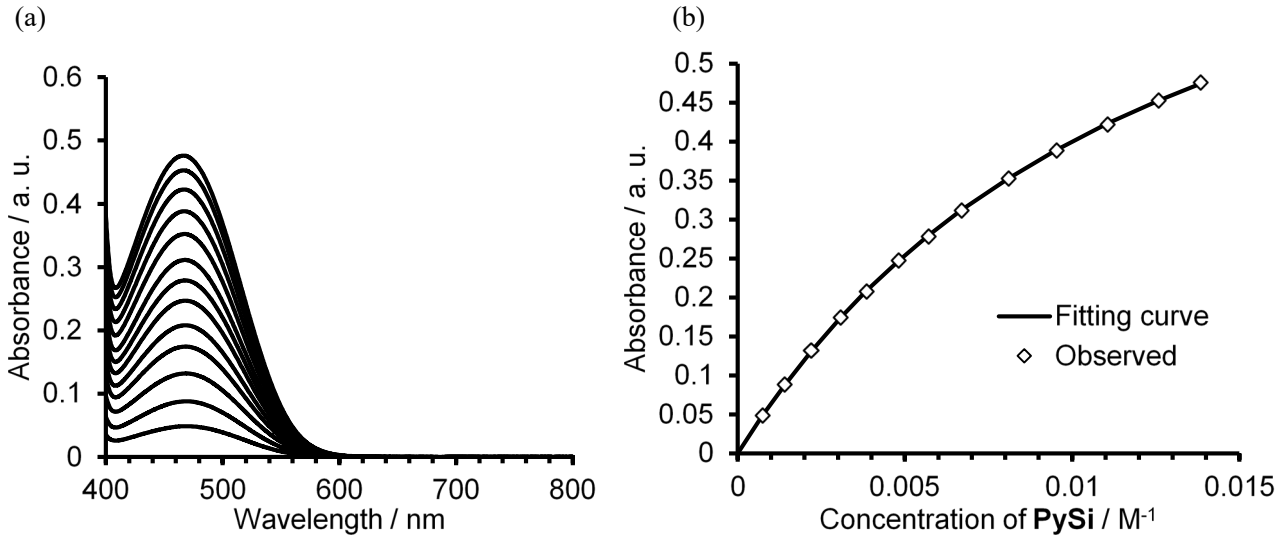


Fig. S27 (a) Absorption spectral variation of **PMDISi-PySi** system in decamethyltetrasiloxane depending on concentration of **PySi**. A solution containing 13.83 mM of **PySi** and 1.87 mM of **PMDISi** in decamethyltetrasiloxane was diluted with 1.87 mM of **PMDISi** in decamethyltetrasiloxane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDISi-PySi** in dodecamethylpentasiloxane

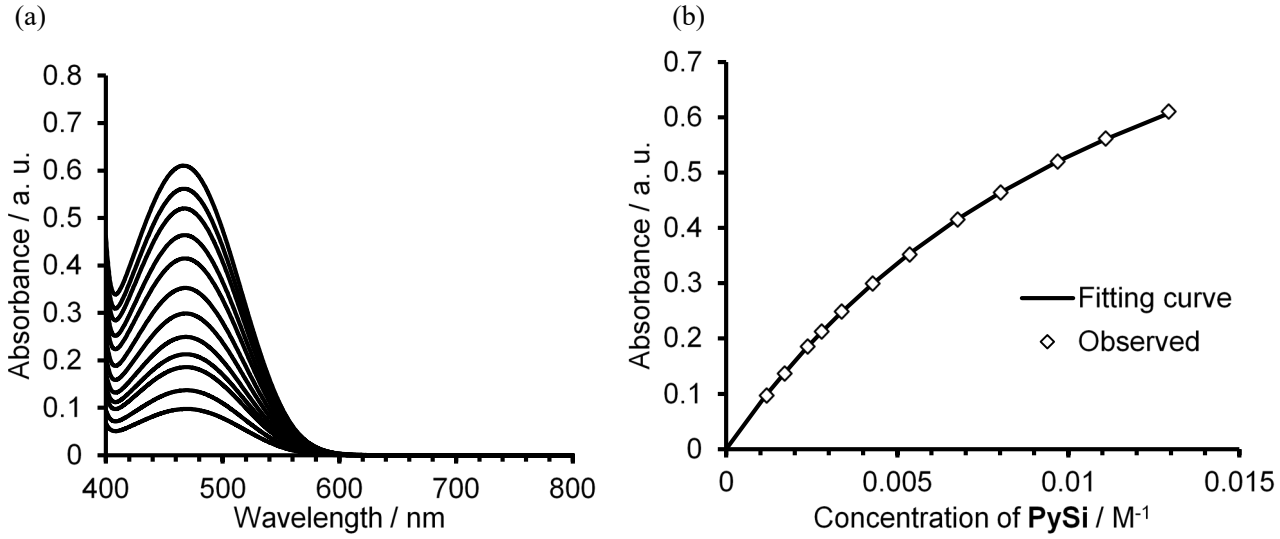


Fig. S28 (a) Absorption spectral variation of **PMDISi-PySi** system in dodecamethylpentasiloxane depending on concentration of **PySi**. A solution containing 12.93 mM of **PySi** and 2.45 mM of **PMDISi** in dodecamethylpentasiloxane was diluted with 2.45 mM of **PMDISi** in dodecamethylpentasiloxane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDISi-PySi** in PDMS(2000)

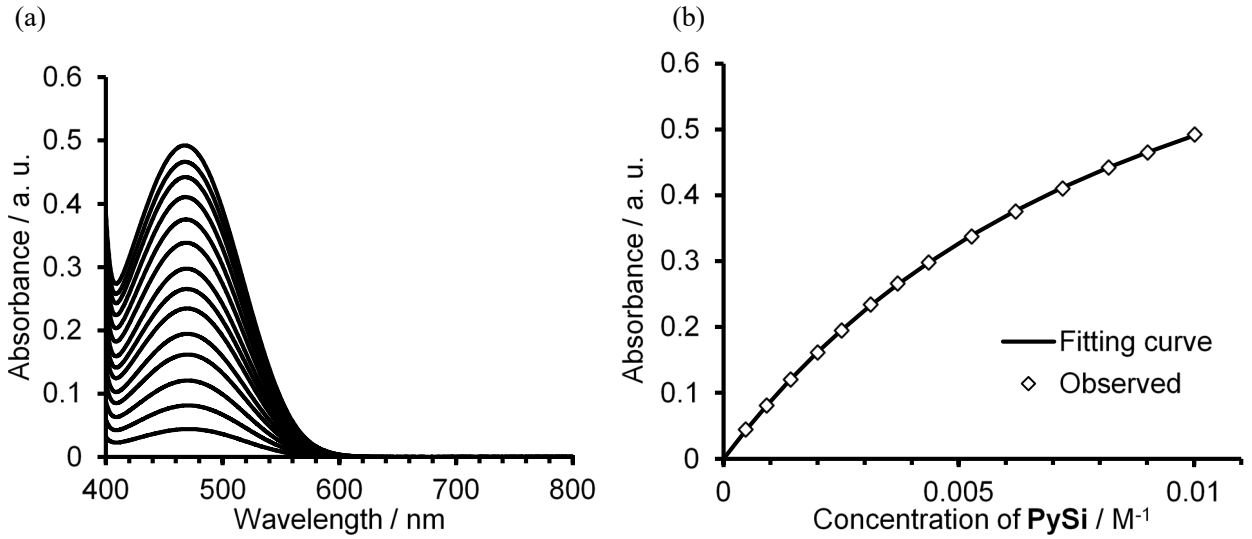


Fig. S29 (a) Absorption spectral variation of **PMDISi-PySi** system in PDMS(2000) depending on concentration of **PySi**. A solution containing 10.00 mM of **PySi** and 1.92 mM of **PMDISi** in PDMS(2000) was diluted with 1.92 mM of **PMDISi** in PDMS(2000). (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDISi-PySi** in PDMS(28000)

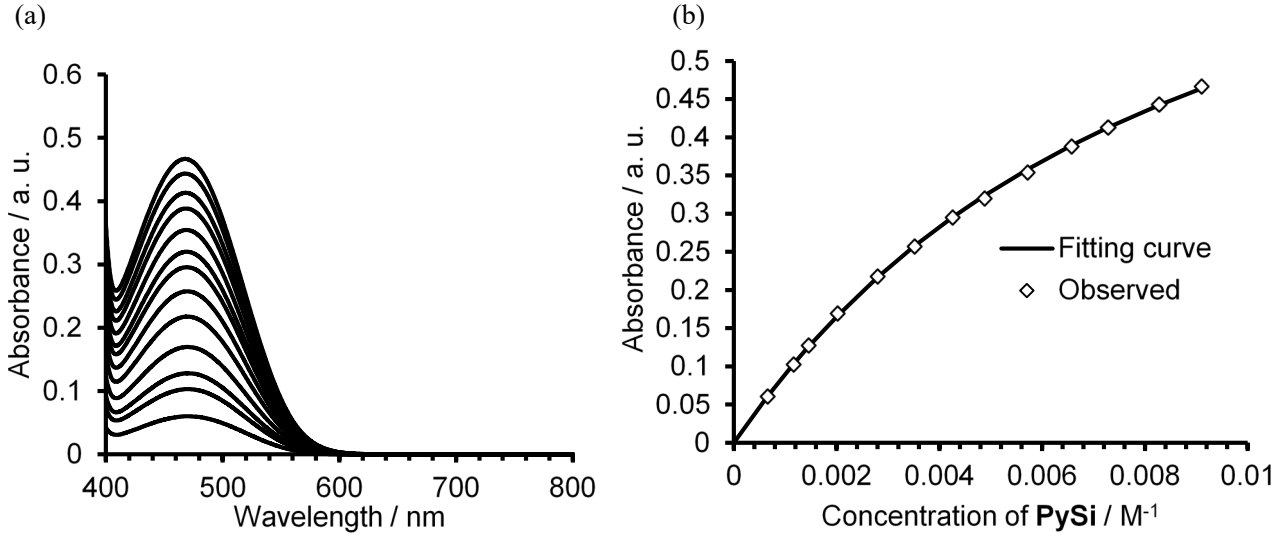


Fig. S30 (a) Absorption spectral variation of **PMDISi-PySi** system in PDMS(28000) depending on concentration of **PySi**. A solution containing 9.10 mM of **PySi** and 1.85 mM of **PMDISi** in PDMS(28000) was diluted with 1.85 mM of **PMDISi** in PDMS(28000). (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PySi** in *n*-hexane

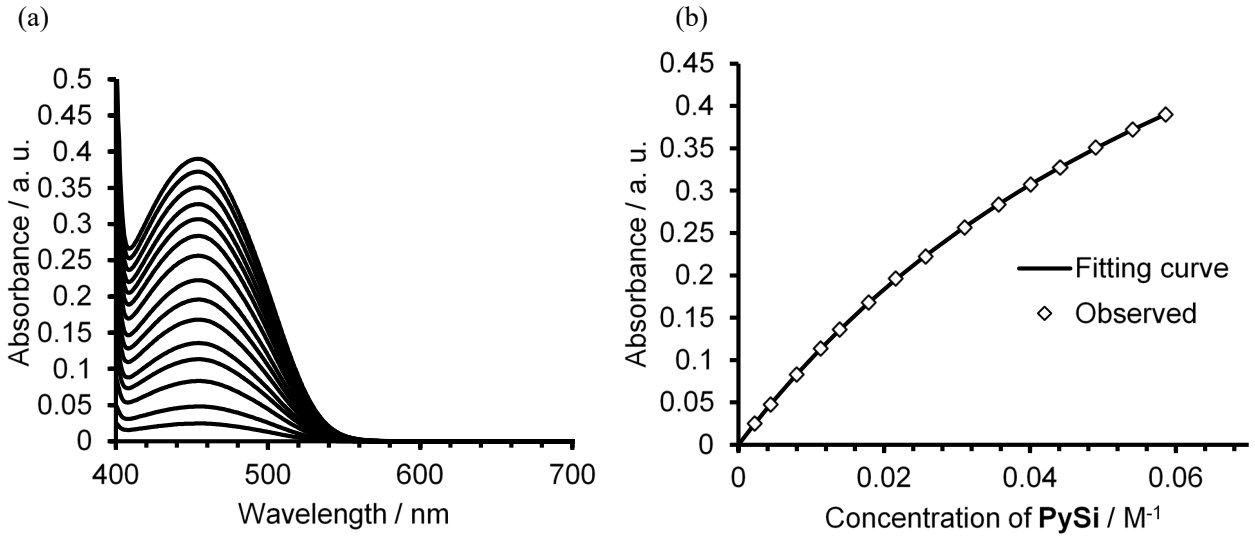


Fig. S31 (a) Absorption spectral variation of **PMDIC6-PySi** system in *n*-hexane depending on concentration of **PySi**. A solution containing 58.60 mM of **PySi** and 2.17 mM of **PMDIC6** in *n*-hexane was diluted with 2.17 mM of **PMDIC6** in *n*-hexane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PySi** in hexamethyldisiloxane

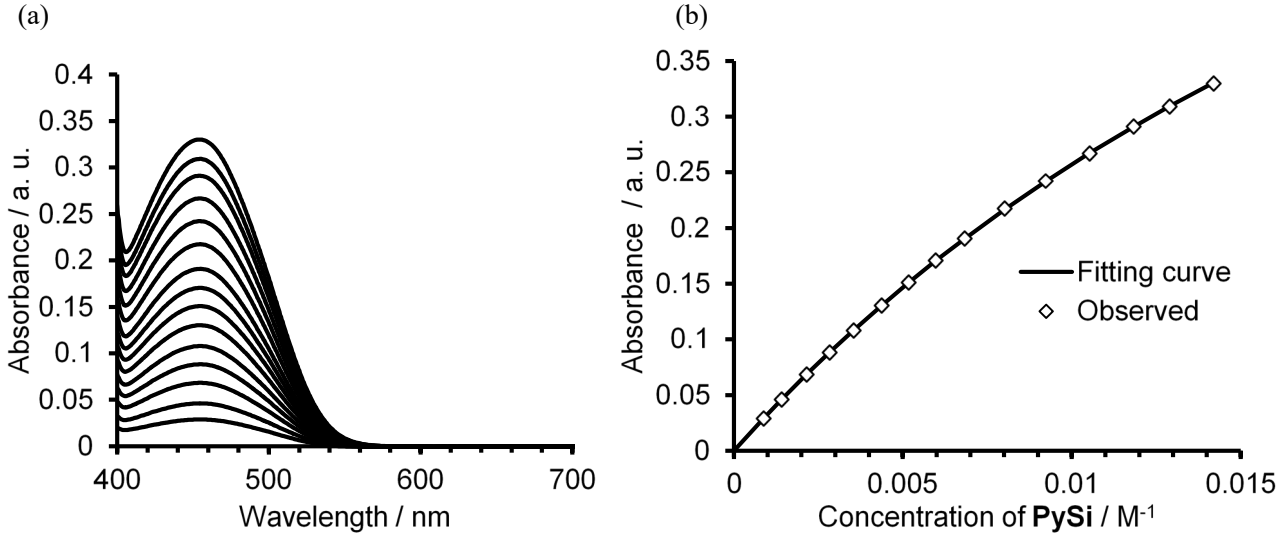


Fig. S32 (a) Absorption spectral variation of **PMDIC6-PySi** system in hexamethyldisiloxane depending on concentration of **PySi**. A solution containing 14.19 mM of **PySi** and 2.35 mM of **PMDIC6** in hexamethyldisiloxane was diluted with 2.35 mM of **PMDIC6** in hexamethyldisiloxane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDIC6-PySi** in PDMS(28000)

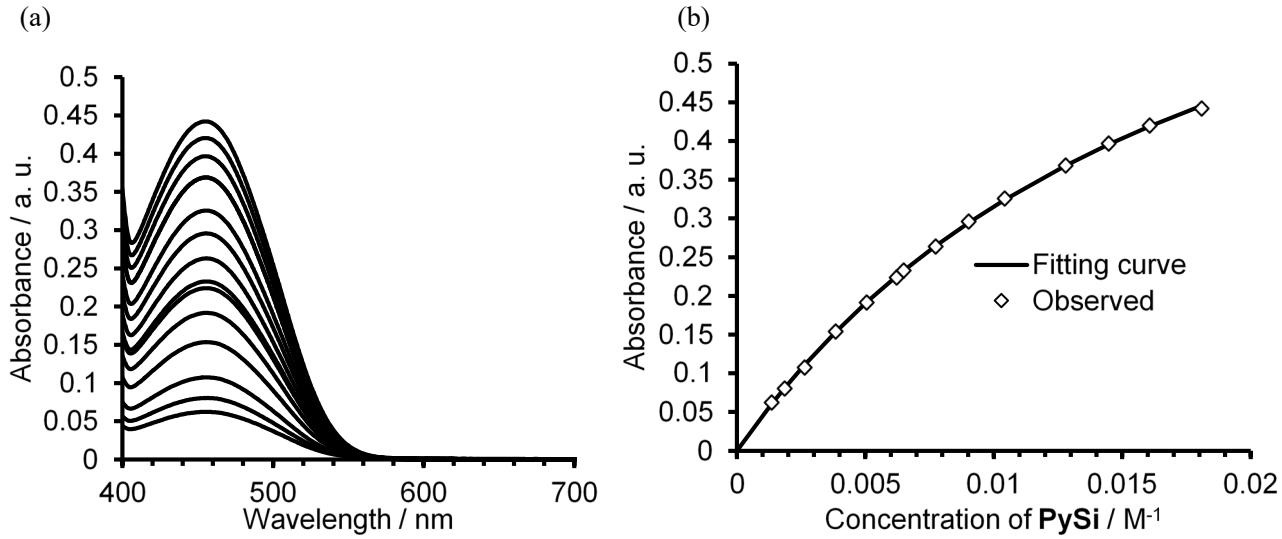


Fig. S33 (a) Absorption spectral variation of **PMDIC6-PySi** system in PDMS(28000) depending on concentration of **PySi**. A solution containing 18.07 mM of **PySi** and 2.10 mM of **PMDIC6** in PDMS(28000) was diluted with 2.10 mM of **PMDIC6** in PDMS(28000). (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDISi-PyC6** in *n*-hexane

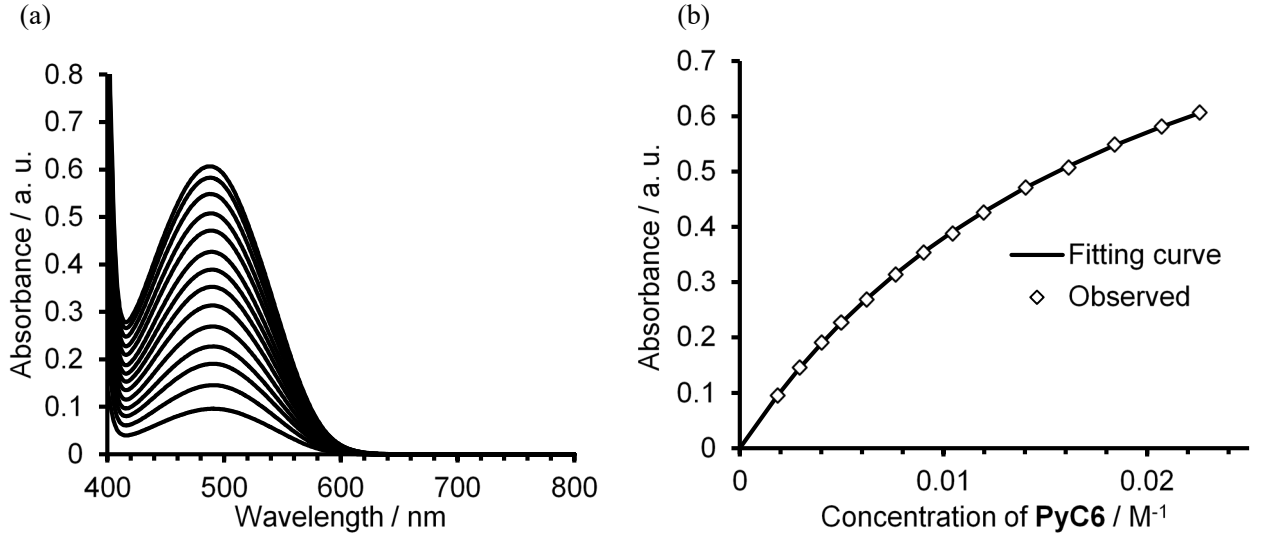


Fig. S34 (a) Absorption spectral variation of **PMDISi-PyC6** system in *n*-hexane depending on concentration of **PyC6**. A solution containing 22.57 mM of **PyC6** and 1.96 mM of **PMDISi** in *n*-hexane was diluted with 1.96 mM of **PMDISi** in *n*-hexane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDISi-PyC6** in hexamethyldisiloxane

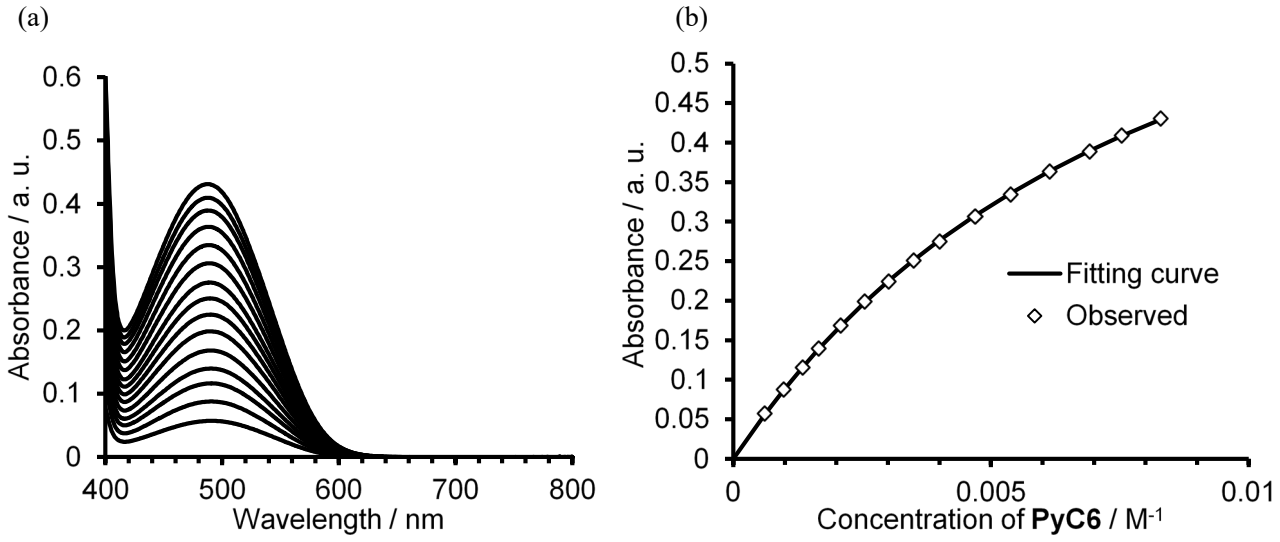


Fig. S35 (a) Absorption spectral variation of **PMDISi-PyC6** system in hexamethyldisiloxane depending on concentration of **PyC6**. A solution containing 8.29 mM of **PyC6** and 1.42 mM of **PMDISi** in hexamethyldisiloxane was diluted with 1.42 mM of **PMDISi** in hexamethyldisiloxane. (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Association constant for **PMDISi-PyC6** in PDMS(28000)

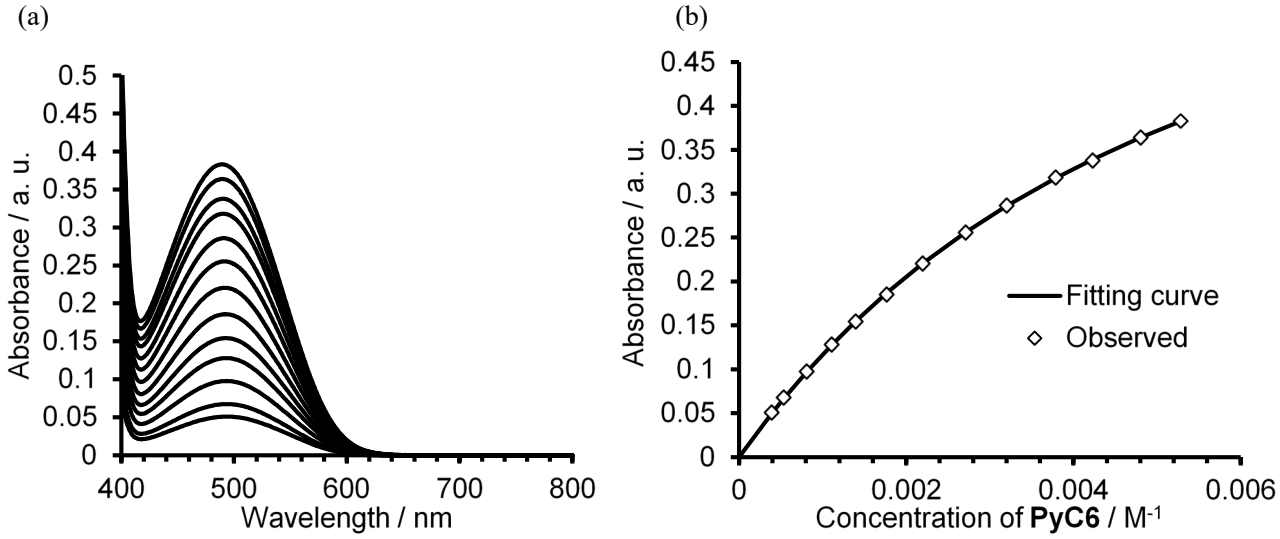


Fig. S36 (a) Absorption spectral variation of **PMDISi-PyC6** system in PDMS(28000) depending on concentration of **PyC6**. A solution containing 5.28 mM of **PyC6** and 1.16 mM of **PMDISi** in PDMS(28000) was diluted with 1.16 mM of **PMDISi** in PDMS(28000). (b) Non-linear curve fitting of the absorbance of charge-transfer absorption.

Solubility test

Solubility of **PMDIC6**, **PyC6**, **PMDISi** and **PySi** at 25 °C were determined by measuring concentration of supernatant or filtrate of suspensions of the chemicals in the solvents, respectively. The suspensions were prepared by left at 25 °C clear solutions of the chemicals obtained by heating. The concentrations were evaluated by using absorption spectroscopy.

Table S1. Solubility (mM) test of **PMDIC6**, **PyC6**, **PMDISi** and **PySi** at 25 °C

Solutes	Solvent							
	Hexane	Hexamethyl disiloxane	Octamethyl trisiloxane	Decamethyl tetrasiloxane	Dodecamethyl pentasiloxane	PDMS (2000)	PDMS (28000)	Bis(trimethylsilyl)methane
PMDIC6	>250 mM[a]	12 mM	7.9 mM	5.6 mM	3.9 mM	2.4 mM	2.0 mM	>250 mM[a]
PyC6	>250 mM[a]	200 mM	150 mM	120 mM	79 mM	52 mM	45 mM	>250 mM[a]
PMDISi	>250 mM[a]	>250 mM[a]	>250 mM[a]	>250 mM[a]	240 mM	47 mM	26 mM	>250 mM[a]
PySi	>250 mM[a]	>250 mM[a]	>250 mM[a]	>250 mM[a]	290 mM	130 mM	110 mM	>250 mM[a]

[a] Precipitation or phase separation at least 250 mM were not observed.

Table S2. The association constants of **PMDIC6-PyC6**, **PMDISi-PySi**, **PMDIC6-PySi** and **PMDISi-PyC6** in *n*-hexane, hexamethyldisiloxane and PDMS(28000) at 25 °C.

	Association constants K_a (M^{-1}) [a]		
	n-hexane	hexamethyldisiloxane	PDMS(28000)
PMDIC6-PyC6	28 (0.4)	88 (1.1)	140 (3.5)
PMDISi-PySi	23 (0.3)	72 (0.9)	140 (3.9)
PMDIC6-PySi	13 (0.2)	37 (0.6)	61 (1.1)
PMDISi-PyC6	55 (0.6)	140 (2.0)	230 (2.8)

[a] Standard error for non-linear least squares in parentheses.

Reference

1. R. D. Rasberry, M. D. Smith and K. D. Shimizu, *Org. Lett.*, 2008, **10**, 2889–2892.

2. J. Maury, D. Mouysset, L. Feray, S. R. A. Marque, D. Siri and M. P. Bertrand, *Chem. - A Eur. J.*, 2012, **18**, 3241–3247.

3. K. Kacprzak, *Synth. Commun.*, 2003, **33**, 1499–1507.