Supplementary Information

# Halogen-Sensitive Solvatochromism Based on

# a Phenolic Polymer of Tetraphenylethene

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# Supporting Information

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# 1. Materials and Measurements.

## Materials

All solvents and reagents were used as supplied without additional purification. We were obtained $TiCl_4$, $AlCl_3$ and benzene from FUJIFILM Wako Pure Chemical Corporation. $Na_2SO_4$ and paraformaldehyde were obtained from Nacalai Tesque Inc. 4,4'-dimethoxybenzophenone, 3,5-dimethyl-4-methoxy-benzoic acid, 2,6-dimethylanisole and $SOCl_2$ were obtained from Tokyo Chemical Industry Co., Ltd. THF, $CH_2Cl_2$, $CH_3OH$, $CH_3COOH$, $CHCl_3$, $K_2CO_3$, zinc powder, sulfuric acid, hydrochloric acid, chloroform-$d_1$, dichloromethane-$d_2$, tetrahydrofuran-$d_8$, dimethyl sulfoxide-$d_6$, silica gel were obtained from Kanto Chemical Co., Inc.

## Measurements

Solution $^1H$ NMR spectra were recorded at 500 MHz with a JEOL‐ECA500 spectrometer. Solution $^{13}C$ NMR spectra were recorded at 125 MHz with a JEOL‐ECA500 spectrometer. 2D NOESY NMR spectra were acquired with a Bruker AVANCE‐400 spectrometer operating at 400 MHz. UV–vis absorption spectra were recorded with a JASCO V‐670 spectrometer. One‐centimeter quartz cuvettes were used for solution absorption. Gel permeation chromatography analysis was performed at 25 °C on a Shodex GPC LF804 system using tetrahydrofuran as the eluent, at a flow rate of 1 mL·min$^{-1}$ after calibration with standard polystyrene samples. FT‐IR spectra were obtained by a JASCO FT‐IR 4100 spectrometer with ATR PRO470-H. Electronic structure calculations were performed with the Gaussian09 program. Molecular geometries were optimized by using DFT with the B3LYP functional and the 3-21G basis set.

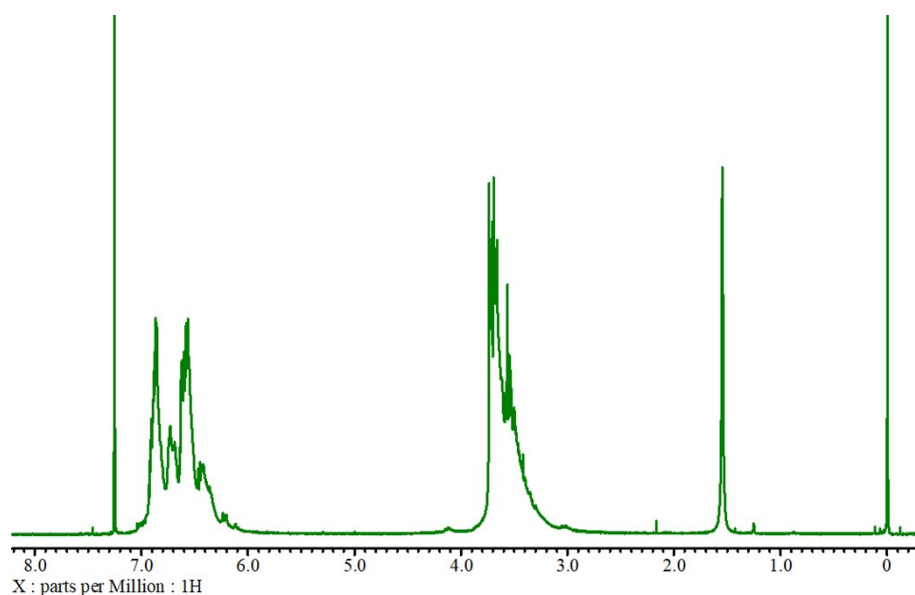## 2. Synthesis of 1,1,2,2-Tetra(4-methoxyphenyl)ethene (TPE-4MeO)[1].

In a three-neck flask under $N_2$ atmosphere, a suspension of zinc powder (4.39 g, 67.2 mmol) in dry THF (140 mL) was prepared and $TiCl_4$ (3.69 mL, 33.6 mmol) was slowly added to the suspension. Subsequently, the suspending mixture was stirred for 2 h, and 4,4'-dimethoxybenzophenone (6.78 g, 28.0 mol) in dry THF (70 mL) was added. After stirring overnight at room temperature, the reaction was quenched with 10 wt% $K_2CO_3$ aqueous solution (240 mL). The mixture was filtered through a celite pad, and the aqueous layer was extracted with $CH_2Cl_2$. After drying over $Na_2SO_4$ and the solvent was evaporated under the reduced pressure. The crude product was recrystallized in $CH_2Cl_2/CH_3OH$ (v/v = 1/2) to yield a white crystalline product (5.59 g, 88.3%). $^1H$ NMR (CHCl$_3$-$d$, 500 MHz), $\delta$ (TMS, ppm): 6.95-6.91 (d,8H, phenyl H), 6.66-6.62 (d, 8H, phenyl H), 3.74 (s, 12H, 4OCH$_3$). $^{13}C$ NMR (CHCl$_3$-$d$, 125 MHz), $\delta$ (TMS, ppm): 55.09, 113.02, 132.54, 136.90, 138.37, 157.78.



X : parts per Million : 1H
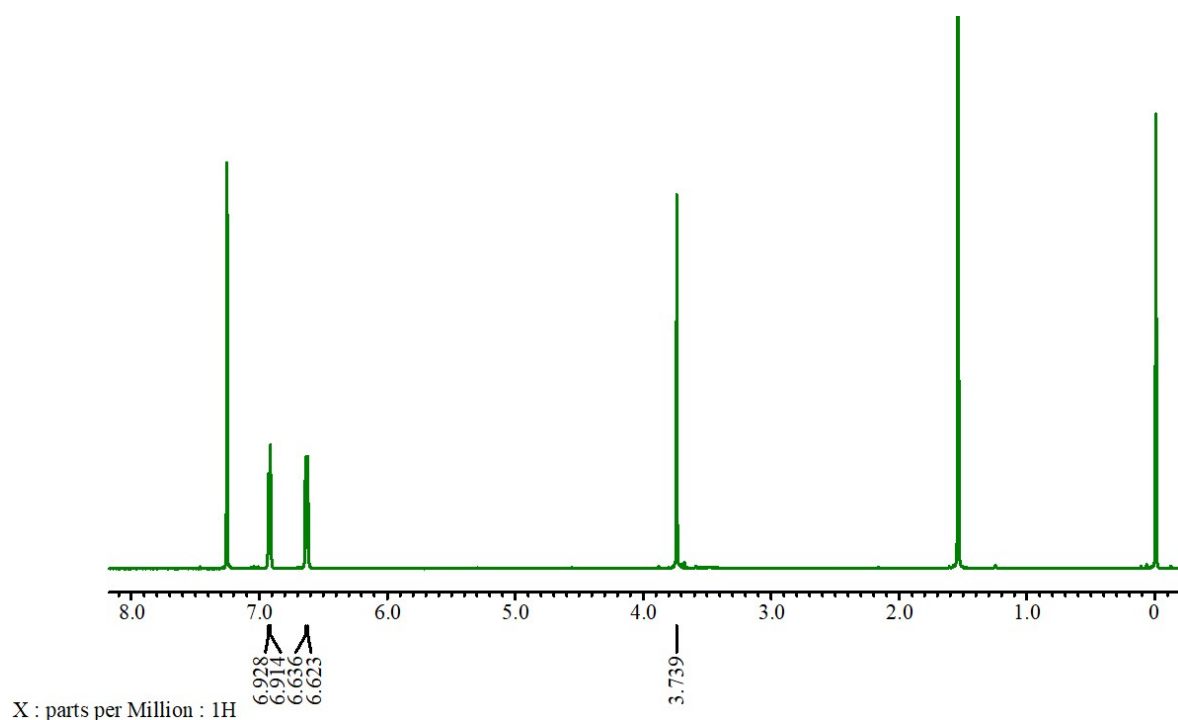
**Figure S1.** $^1H$ NMR spectrum of TPE-4MeO (CHCl$_3$-$d$, 500 MHz, 303K).

### 3. Polymerization of TPE-4MeO and Characterizations of TPE-P.

In 50 mL of recovery flask, TPE-4MeO (2.26 g, 5.00 mmol) and paraformaldehyde (0.15 g, 5.00 mmol as formaldehyde) were dissolved in $CH_3COOH/CHCl_3$ (v/v = 1:1, 20 mL) at 80 °C. Concentrated sulfuric acid (1.24 mL) in mixed solvent of $CH_3COOH/CHCl_3$ (5 mL) was added dropwise, and the mixture was refluxed for 19 h. After cooling to room temperature, the solution was poured to 250 mL of cold methanol to precipitate. The precipitated TPE-P was washed with water several times and then dried. Yield: 1.89 g (78.5%).



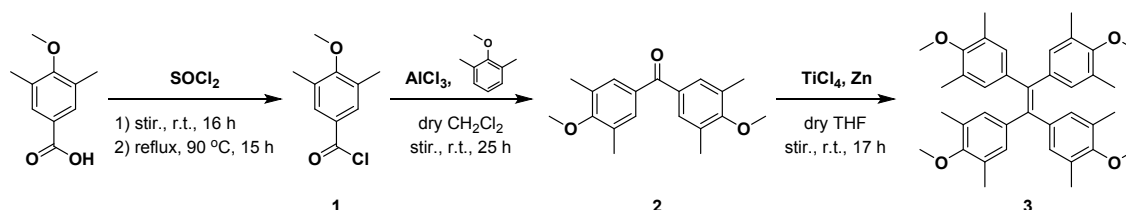**Figure S2.** $^1H$ NMR spectrum of TPE-P (CHCl$_3$-*d*, 500 MHz, 303K).
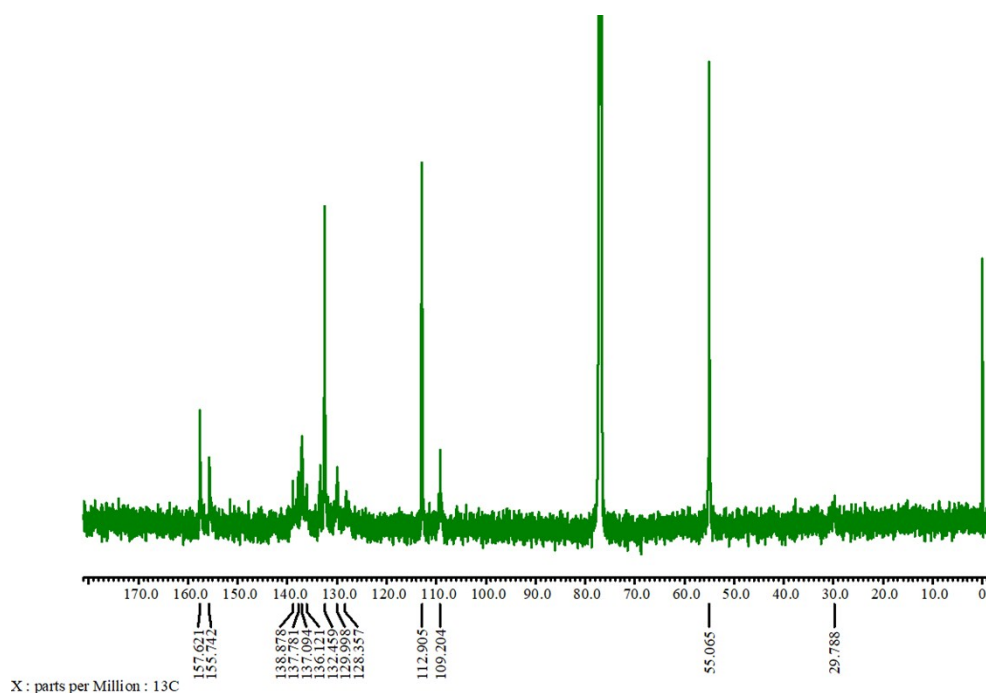


**Figure S3.** $^{13}C$ NMR spectrum of TPE-P (CHCl$_3$-*d*, 125 MHz, 303K).

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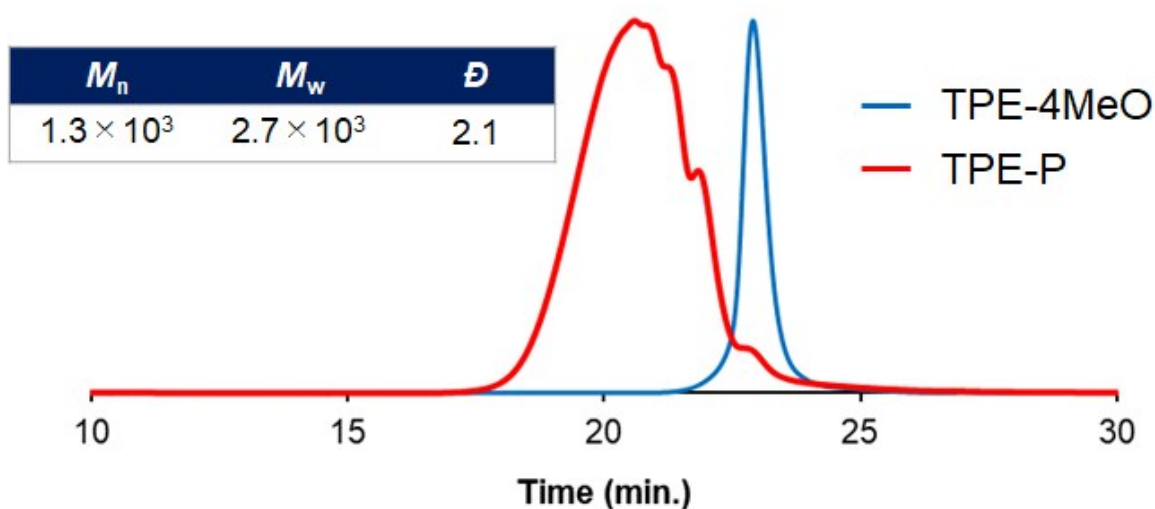
**Figure S4.** GPC measurements of TPE-4MeO and TPE-P.

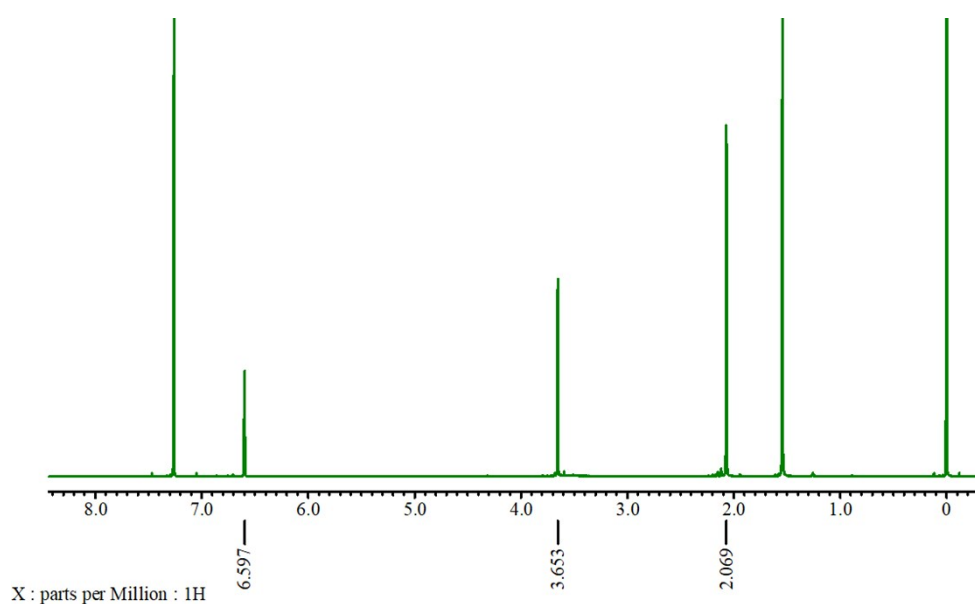## 4. Synthesis of 1,1,2,2-tetrakis(4-methoxy-3,5-dimethylphenyl)ethene (3).
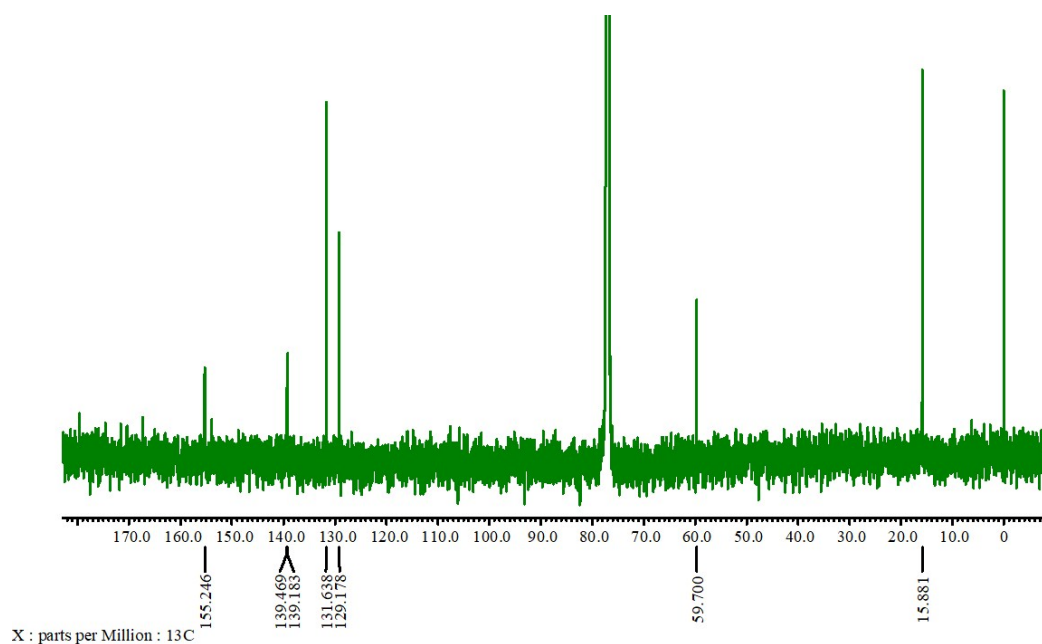


**Bis(4-methoxy-3,5-dimethylphenyl)methanone (2)**.

3,5-dimethyl-4-methoxy-benzoic acid (0.500 g, 2.77 mmol) was dissolved in SOCl$_2$ (10.0 mL) and stirred at room temperature for 16 h and then heated to reflux for 15 h. Next, SOCl$_2$ was evaporated under the reduced pressure and azeotroped twice with benzene to give 1. The compound 1 as crude and AlCl$_3$ (0.49 g, 3.67 mmol) were dissolved in dry CH$_2$Cl$_2$ (10 mL). 2,6-dimethylanisole (0.39 mL, 2.77 mmol) was then added dropwise to the suspension. The stirring was continued overnight, and the solution was carefully poured into water and decanted. The aqueous layer was extracted with CH$_2$Cl$_2$ and the combined organic layers were washed with water, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The crude mixture was separated on a silica gel column with CH$_2$Cl$_2$ as an eluent to yield a white crystalline product (0.38 g, 46.0%). $^1$H NMR (CHCl$_3$-$d$, 500 MHz), $\delta$ (TMS, ppm): 7.46 (s,4H, phenyl H), 3.79 (s, 6H, 2OCH$_3$), 2.33 (s, 12H, 4Ar-CH$_3$). Spectral data was found to be consistent with those reported.[2]

**1,1,2,2-Tetra(4-methoxy-3,5-dimethylphenyl) ethene (3)**.

In a three-neck flask under $N_2$ atmosphere, a suspension of zinc powder (0.20 g, 3.10 mmol) and 2 (0.38 g, 1.3 mmol) in dry THF (10 mL) was prepared and $TiCl_4$ (0.17 mL, 1.55 mmol) was slowly added to the suspension at 0 °C. After stirring overnight at room temperature, the reaction was quenched with 10 wt% $K_2CO_3$ aqueous solution (20 mL). The mixture was filtered through a celite pad, and the aqueous layer was extracted with $CH_2Cl_2$. After drying over $Na_2SO_4$ and the solvent was evaporated under the reduced pressure. The crude product was recrystallized in $CH_2Cl_2/CH_3OH$ (v/v = 1/2) to yield a white crystalline product (0.25 g, 68.2%). $^1H$ NMR (CHCl$_3$-$d$, 500 MHz), $\delta$ (TMS, ppm): 6.60 (s,8H, phenyl H), 3.65 (s, 12H, 4OCH$_3$), 2.07 (s, 24H, 8Ar-CH$_3$). $^{13}C$ NMR (CHCl$_3$-$d$, 125 MHz), $\delta$ (TMS, ppm): 15.88, 59.70, 129.18, 131.64, 139.18, 139.47, 155.25.



**Figure S5.** $^1H$ NMR spectrum of 1,1,2,2-tetrakis(4-methoxy-3,5-dimethylphenyl)ethene. (CHCl$_3$-$d$, 500 MHz, 303K).
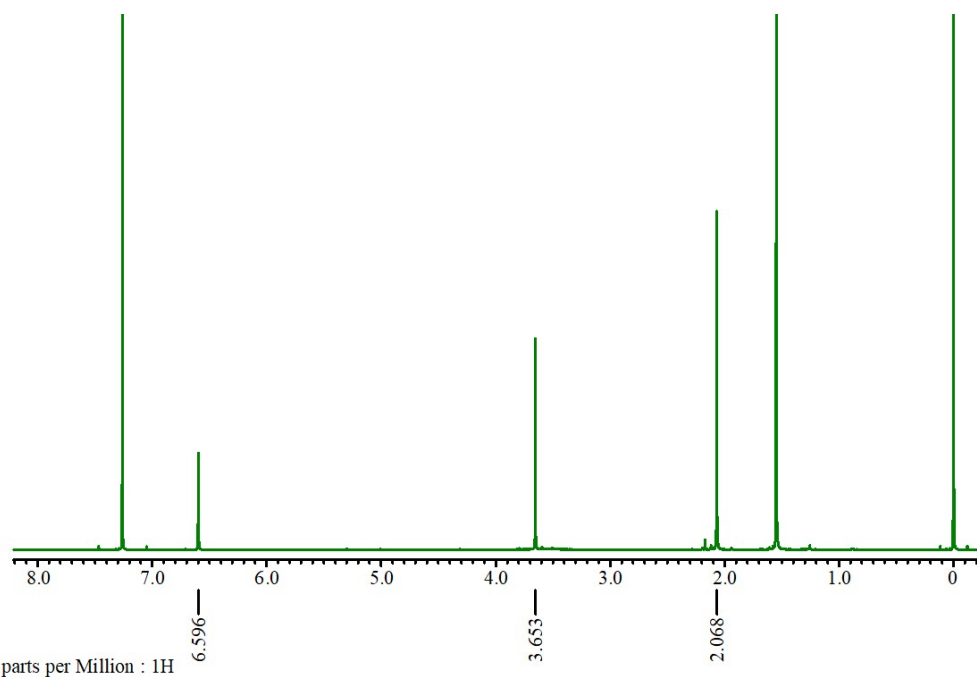
**Figure S6.** $^{13}C$ NMR spectrum of 1,1,2,2-tetrakis(4-methoxy-3,5-dimethylphenyl)ethene (CHCl$_3$-$d$, 125 MHz, 303K).

## 5. Polymerization of 1,1,2,2-tetrakis(4-methoxy-3,5-dimethylphenyl)ethene.

In 50 mL of recovery flask, 3 (226 mg, 0.40 mmol) and paraformaldehyde (12.0 mg, 0.40 mmol as formaldehyde) were dissolved in CH$_3$COOH/CHCl$_3$ (v/v = 1:1, 10 mL) at 80 °C. Concentrated sulfuric acid (413 µL) in mixed solvent of CH$_3$COOH/CHCl$_3$ (2 mL) was added dropwise, and the mixture was refluxed for 19 h. After cooling to room temperature, the reaction was quenched with saturation NaHCO$_3$ aqueous solution, and the aqueous layer was extracted with CH$_2$Cl$_2$. After drying over Na$_2$SO$_4$ and the solvent was evaporated under the reduced pressure. The crude product was recrystallized in CH$_2$Cl$_2$/CH$_3$OH (v/v = 1/2) to yield a white crystalline product (106 mg, 47.2%).
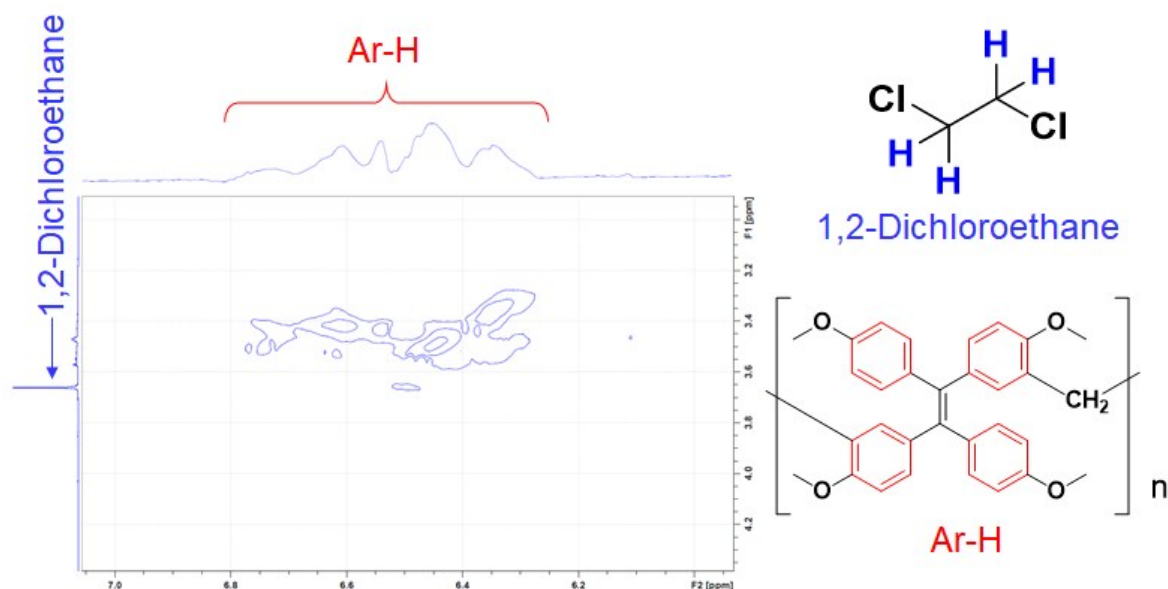
**Figure S7.** $^1$H NMR spectrum of polymerized 1,1,2,2-tetrakis(4-methoxy-3,5-dimethylphenyl)ethene. (CHCl$_3$-*d*, 500 MHz, 303K).

## 6.   2D NOESY Spectrum between TPE-P and 1,2-Dichloroethane.

2D NOESY spectrum was recorded by mixing the TPE-P and 1,2-dichloroethane (1 : 1 mol%) in THF-$d_8$. Peak of 1,2-dichloroethane was correlated with aromatic peaks of TPE-P.



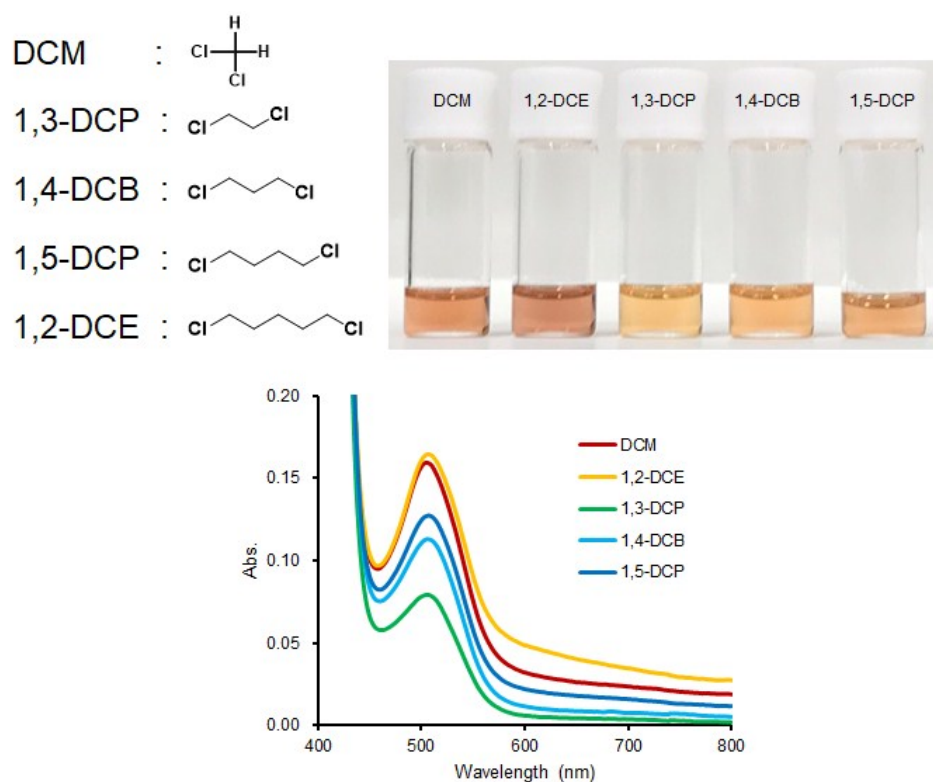**Figure S8.** $^1$H-$^1$H 2D NMR spectrum (THF-$d_8$, 400 MHz, 303K).

## 7.   The Effect of Free Anion on Solvatochromism.

Free anion effect was investigated by mixing the tetrabutylammonium anions to TPE-P solution in 1,4-dioxane at 20 mg/mL.
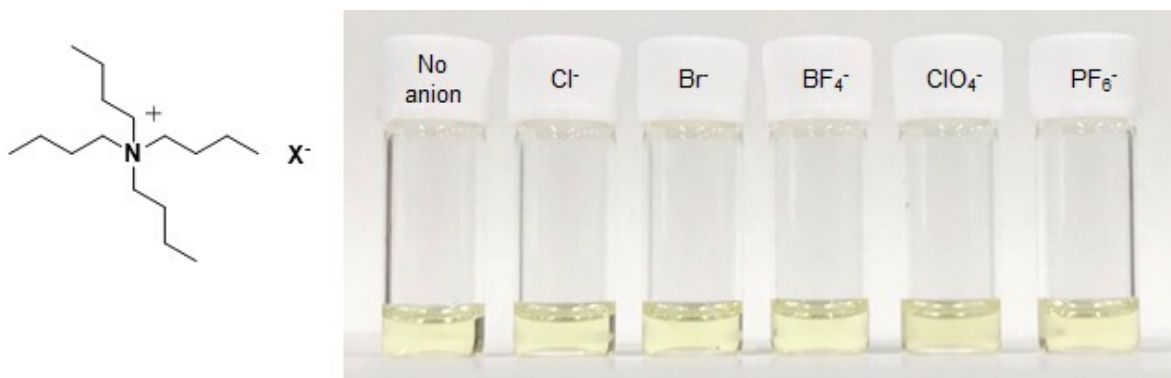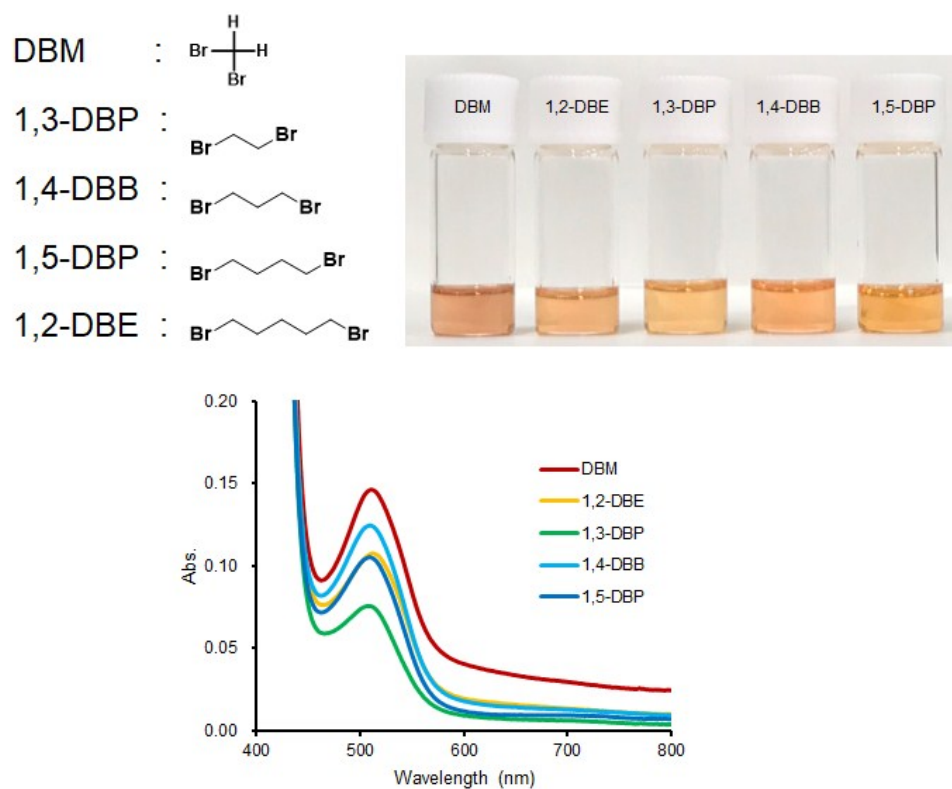


**Figure S9.** Photo images for mixture of TPE-P and free anions in the 1,4-Dioxane.

**8.  The dependency on alkyl chain length of guest molocules.**



**Figure S10.** UV-Vis absorption spectra of TPE-P in various dichloroalkanes.



**Figure S11.** UV-Vis absorption spectra of TPE-P in various dibromoalkanes.

## 9.  Measurements of Binding Constant.

Binding constants were calculated by the Hill's equation. The Hill's equation is used to describe the fraction of a macromolecule saturated by ligand as a function of the ligand concentration. The linearized Hill equation is described as below.

$$Y = \frac{[L]^n}{(K_D)^n + [L]^n}$$

The equation's terms are defined as follows: $Y$ is fraction of the receptor protein concentration that is bound to ligand. $[L]$ is free (unbound) ligand concentration. $K_D$ is apparent dissociation constant derived from the law of mass action (the equilibrium constant for dissociation). $K_D$ is the ligand concentration producing half occupation (ligand concentration occupying half of the binding sites). $n$ is the Hill coefficient. $n > 1$: Positively cooperative binding: Once one ligand molecule is bound to the enzyme, its affinity for other ligand molecules increases. $n < 1$: Negatively cooperative binding: Once one ligand molecule is bound to the enzyme, its affinity for other ligand molecules decreases. Taking the logarithm of both sides of the equation leads to an alternative formulation of the Hill equation:
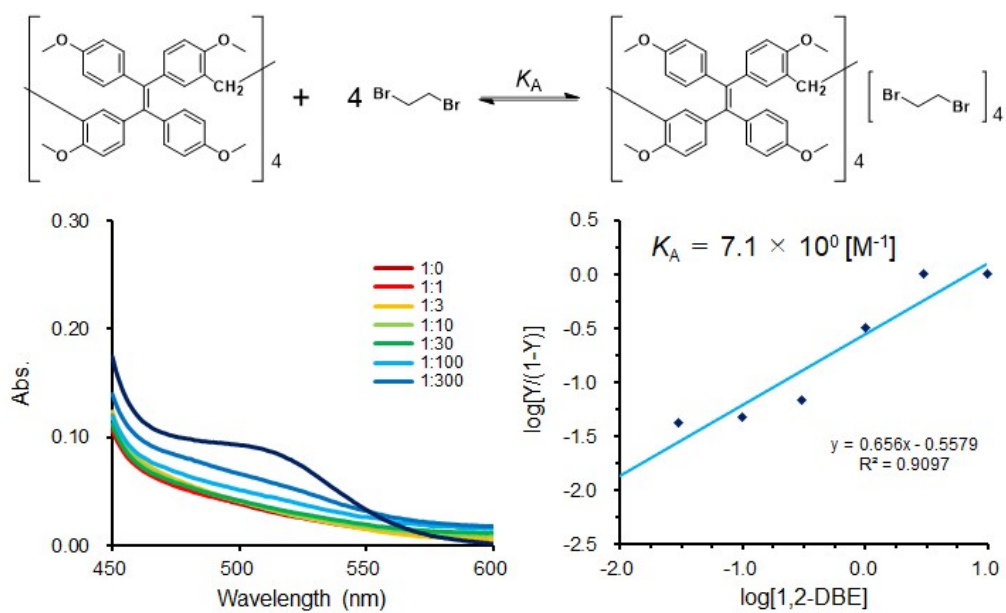
$$log\left(\frac{Y}{1-Y}\right) = n\,log[L] - n\,logK_D$$

A plot of $log\left(\dfrac{Y}{1-Y}\right)$ versus $log[L]$ yield a linear plot, which is called Hill's plot.

$$K_D = \frac{1}{K_A}$$
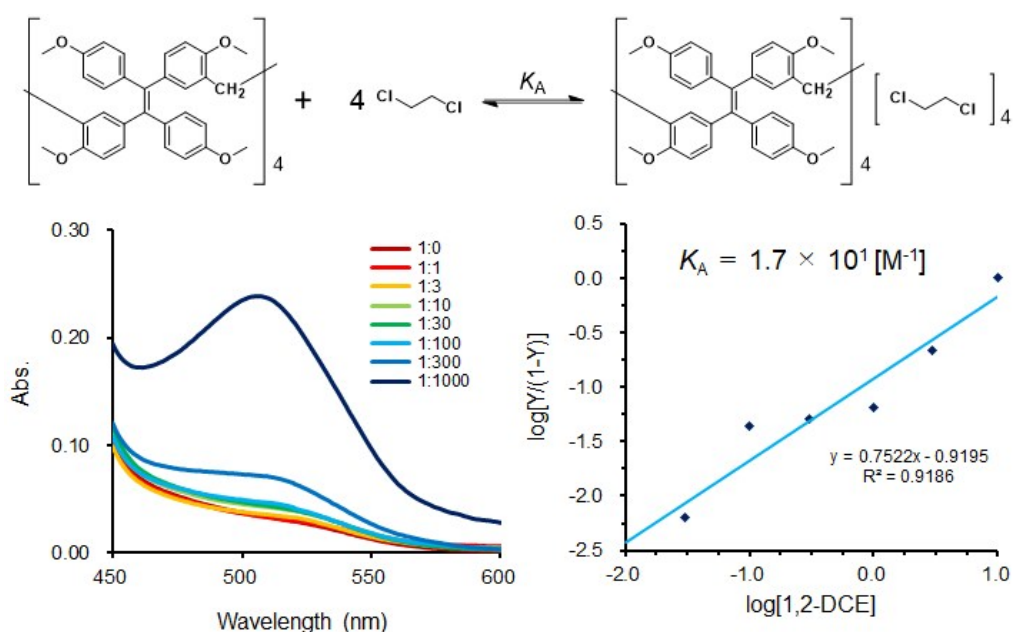
**Figure S12.** The binding constant between TPE-P and 1,2-DCE.



**Figure S13.** The binding constant between TPE-P and 1,2-DBE.

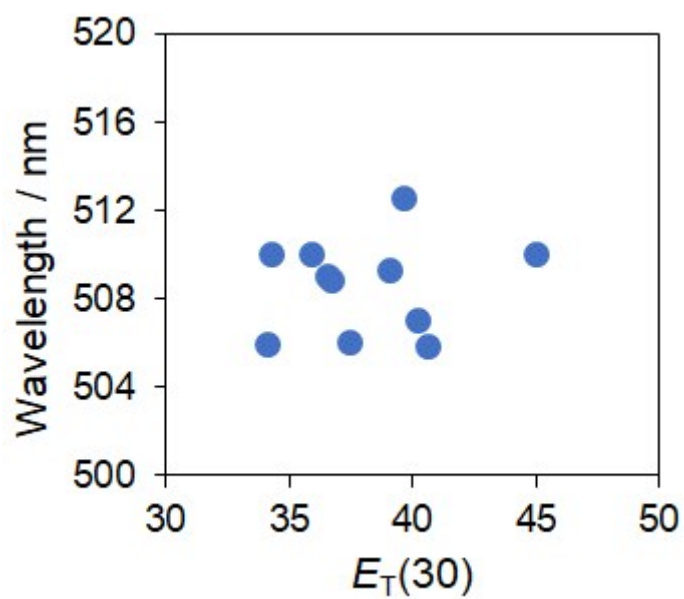## 10. The relationships of dielectric constant.



**Figure S14.** The dependency on dielectric constant of solvents.

## 11. References

(1)   H. Jing, L. Lu, Y. Feng, J.-F. Zheng, L. Deng, E.-Q. Chen and X.-K. Ren, *The Journal of Physical Chemistry C*, 2016, **120**, 27577-27586.

(2)   T. E. Hurst, J. A. Deichert, L. Kapeniak, R. Lee, J. Harris, P. G. Jessop and V. Snieckus, *Organic Letters*, 2019, **21**, 3882-3885.

(3)   J. P. Cerón-Carrasco, D. Jacquemin, C. Laurence, A. Planchat, C. Reichardt and K. Sraïdi, *Journal of Physical Organic Chemistry*, 2014, **27**, 512-518.