Supporting Information

## Multiphase Behavior of Tetraphenylethylene Derivatives with Different Polarities at High Pressures

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## Estimation of the concentrations of TPE1H and TPE2H<sub>2</sub> species in the aqueous phase

The concentrations of TPE species in the aqueous phase shown in Figure 5 in the main text were calculated in the following way. Although only the estimation of the concentrations of TPE1H-related species is shown here, the same scheme is applicable to TPE2H<sub>2</sub>.

In the present study, the distribution ratio was determined by UV absorption in the organic phase. From the distribution ratios, the concentration of free TPE1<sup>-</sup> in the aqueous phase containing  $\gamma$ -CD is given by

$$\left[\text{TPE1}^{-}\right]_{W} = \frac{c_{0}^{\text{TPE1H}} D_{CD}^{\text{TPE1}} \ 1}{1 + D_{CD}^{\text{TPE1}} \ D^{\text{TPE1}}},$$
(S1)

where  $c_0^{\text{TPE1H}}$  is the initial concentration of TPE1H added to the organic phase. The concentration of the  $\gamma$ -CD complex of TPE1<sup>-</sup> was calculated from [TPE1<sup>-</sup>]<sub>W</sub>,

$$K_{\text{CD1}} = \frac{[\text{TPE1}^{\circ}\text{CD}]_{\text{W}}}{[\text{TPE1}^{\circ}]_{\text{W}}[\text{CD}]_{\text{W}}} = \frac{[\text{TPE1}^{\circ}\text{CD}]_{\text{W}}}{[\text{TPE1}^{\circ}]_{\text{W}}([\text{CD}]_{\text{W}}^{\text{ini}} - [\text{TPE1}^{\circ}\text{CD}]_{\text{W}})},$$
(S2)

$$[\text{TPE1}^{-}\text{CD}]_{W} = \frac{K_{\text{CD1}}[\text{TPE1}^{-}]_{W}c_{W}^{\text{CD}}}{1 + K_{\text{CD1}}[\text{TPE1}^{-}]_{W}c_{W}^{\text{CD}}},$$
(S3)

where  $c_{W}^{CD}$  is the initial concentration of  $\gamma$ -CD in the aqueous phase. Thus, the

concentration of TPE1<sup>-</sup> in the aggregate (
$$[aggTPE1^{-}]_{W}$$
) is given by

$$\left[ \text{aggTPE1}^{-} \right]_{W} = \frac{c_{0}^{\text{TPE1H}}}{1 + D_{\text{CD}}^{\text{TPE1}}} - \left[ \text{TPE1}^{-} \right]_{W} - \left[ \text{TPE1}^{-} \text{CD} \right]_{W}.$$
(S4)

Table S1 Provisional  $K_{CD1}$  and  $K_{CD2}$  values at 0.1, 160, and 320 MPa determined by

	P/MPa	$K_{\rm CD1}/10^3$	$K_{\rm CD2}/10^3$
TPE1	0.1	3.03	10.6
	160	6.03	6.52
	320	23.9	2.01
TPE2	0.1	5.68	0.911
	160	3.08	1.55
	320	1.11	4.64

curve-fitting assuming 1:1 and 1:2 complexation, as shown in Figure S3.



Figure S1 <sup>1</sup>H NMR spectra (400 MHz) of (a) TPE1H in CDCl<sub>3</sub> and (b) TPE2H<sub>2</sub> in deuterated dimethyl sulfoxide (DMSO- $d_6$ ). For TPE1H: (observed)  $\delta$  8.34 (s), 7.72 (d, J = 8.5 Hz, 2H), 7.18–6.99 (m, 17H); (reported)<sup>1</sup>  $\delta$  7.85–7.80 (d, 2H), 7.16–7.09 (m, 11H), 7.07–7.01 (m, 6H) in CDCl<sub>3</sub>. For TPE2H<sub>2</sub>: (observed)  $\delta$  7.71 (d, J = 8.6 Hz, 4H), 7.16–7.08 (m, 10 H), 7.00–6.98 (m, 4H); (reported)<sup>2</sup>  $\delta$  7.82 (AA'BB', J = 8.4 Hz, 4H), 7.81 (AA'BB', J = 8.4 Hz, 4H), 7.20–7.15 (m, 20H), 7.09–7.06 (m, 8H) in acetone- $d_6$ .



Figure S2. Schematic representation of the pressure apparatus and cell. The yellow ellipse in the cell represents the area for the passage of incident light.



Figure S3 UV spectra, CD spectra, and *g* factor for the complexes of  $\gamma$ -CD and TPE1(A) and for the complexes of  $\gamma$ -CD and TPE2 (B).



Figure S4 Calculated dipole moment of TPE1 at the semi-empirical PM7 level of theory calculated using MOPAC 2016 (A) and schematic representation of the complex of TPE1 and  $\gamma$ -CD according to the sector rule (B).



Figure S5 Calculated dipole moment of TPE2 at the semi-empirical PM7 level of theory calculated using MOPAC 2016 (A) and schematic representation of the complex of TPE2 and  $\gamma$ -CD according to sector rule (B).

## Reference

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2. Nakamura, M.; Sanji, T.; Tanaka, M., Fluorometric Sensing of Biogenic Amines with Aggregation-Induced Emission-Active Tetraphenylethenes. *Chemistry* **2011**, *17*, 5344-5349.