Supporting Information

for

Nanoconfinement of Tetraphenylethylene in Zeolitic Metal-Organic Framework for Turn-on Mechanofluorochromic Stress Sensing

Yang Zhang, a Tao Xiong, a Annika F. Möslein, a Samraj Mollick, a Vishal Kachwal, a
Arun Singh Babal, a Nader Amin, b and Jin-Chong Tan a

Multifunctional Materials & Composites (MMC) Laboratory, Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, U.K.

Department of Chemistry, University of Oxford, Mansfield Road, Oxford OX1 3TA, U.K.

*Corresponding author
E-mail: jin-chong.tan@eng.ox.ac.uk
Figure S1. DFT simulation results of TPE monomer and its vibrations at 1073.98 cm\(^{-1}\), 1233.80 cm\(^{-1}\), 1436.83 cm\(^{-1}\), and 1485.72 cm\(^{-1}\). The infrared vibrational frequencies are obtained at the B3LYP/6-311G* level of theory and implementing an empirical scaling factor of 0.97.
Figure S2. ATR-FTIR spectra of TPE, TPE@ZIF-71 and ZIF-71. The predicted TPE spectrum was obtained from DFT calculations at the B3LYP/6-311G* level of theory and implementing an empirical scaling factor of 0.97.
Figure S3. TGA results of TPE, TPE@ZIF-71 and ZIF-71. The wt.% of TPE : ZIF-71 = (97.181 – 96.944) : 96.944 = 0.237 : 96.944
Figure S4. Solution $^1$H NMR of TPE@ZIF-71 where the guest/host peaks used for integration are indicated as TPE and dclm, respectively. The guest loading calculated is 1 TPE for every 146 cages of ZIF-71.
Figure S5. The configuration of the TPE dimer calculated from DFT simulation and its maximum molecular size. The structure is obtained at the B3LYP-D3/6-311G* level of theory.
**Figure S6.** TPE/ZIF-71 pellet prepared using a physically-mixed powder of TPE and ZIF-71, and TPE@ZIF-71 pellet prepared under a nominal pressure of 346.6 MPa, their colors viewed in ambient light, and their fluorescence observed under a 365-nm UV lamp. The wt.% of TPE and ZIF-71 used to prepare the physically-mixed samples was based on the TGA results in Figure S3. Blue dots in the physically-mixed powders indicate the TPE molecules are not distributed uniformly, resulting in closer intermolecular interactions and a feeble caging effect, which allows for additional nonradiative decay channels and gives weak emission after pressure.
Figure S7. Peak positions of TPE@ZIF-71 and its pellets in the region of 490 – 590 cm$^{-1}$, as determined from Gauss fittings (in OriginPro).
Figure S8. Upper row: XRD patterns of TPE@MIL-68(In) and TPE@UiO-67; Lower row: TPE@MIL-68(In), TPE@UiO-67, and TPE@ZIF-71 pellets prepared under a nominal pressure of 346.6 MPa, their colors viewed in visible light (left), and their fluorescence under a 365 nm UV lamp (right).
Figure S9. Turn-on type mechanofluorochromic behavior of TPE@ZIF-71/PU fibers and TPE@ZIF-71/PVDF membranes. Note: the samples here are to demonstrate its sensing properties and engineering application potential. More rigorous research will be conducted as follow-on studies.
Table S1. Values of time constants ($\tau_i$), normalized pre-exponential factors ($a_i$), and fractional contributions ($c_i = \tau_i \cdot a_i$) of the emission decay of TPE suspension, ZIF-71 and TPE@ZIF71 powders upon excitation at 362.5 nm ($R_t = \Sigma a_i e^{(-t/\tau_i)}$, $R_t$ is the quantity/counts at time $t$).

| Sample       | $\lambda_{\text{obs}}$ [nm] | $\tau_1$ [ns] | $a_1$  | $c_1$ [%] | $\tau_2$ [ns] | $a_2$  | $c_2$ [%] | $\tau_3$ [ns] | $a_3$  | $c_3$ [%] | $\chi^2$ |
|--------------|-----------------------------|---------------|--------|-----------|---------------|--------|-----------|---------------|--------|-----------|----------|
| TPE          | 450                         | 0.71          | 0.029  | 12.85     | 2.44          | 0.027  | 40.94     | 5.77          | 0.013  | 46.21     | 1.098    |
|              | 460                         | 0.71          | 0.024  | 9.40      | 2.44          | 0.028  | 37.18     | 5.77          | 0.017  | 53.43     | 1.132    |
|              | 470                         | 0.71          | 0.020  | 7.78      | 2.44          | 0.025  | 32.99     | 5.77          | 0.019  | 59.23     | 1.119    |
|              | 480                         | 0.71          | 0.019  | 6.74      | 2.44          | 0.023  | 29.22     | 5.77          | 0.022  | 64.05     | 1.087    |
|              | 490                         | 0.71          | 0.017  | 5.71      | 2.44          | 0.022  | 25.55     | 5.77          | 0.025  | 68.74     | 1.111    |
| ZIF-71       | 427                         | 0.49          | 0.072  | 37.08     | 1.75          | 0.027  | 50.06     | 4.79          | 0.003  | 12.86     | 1.154    |
|              | 437                         | 0.49          | 0.066  | 33.48     | 1.75          | 0.029  | 51.67     | 4.79          | 0.003  | 14.85     | 1.144    |
|              | 447                         | 0.49          | 0.062  | 29.73     | 1.75          | 0.031  | 52.26     | 4.79          | 0.004  | 18.01     | 1.116    |
|              | 457                         | 0.49          | 0.060  | 27.98     | 1.75          | 0.030  | 50.66     | 4.79          | 0.005  | 21.36     | 1.097    |
|              | 467                         | 0.49          | 0.056  | 25.09     | 1.75          | 0.032  | 50.64     | 4.79          | 0.006  | 24.27     | 1.110    |
| TPE@ZIF-71   | 426                         | 0.49          | 0.062  | 33.43     | 1.75          | 0.029  | 51.61     | 4.79          | 0.003  | 14.96     | 1.136    |
|              | 436                         | 0.49          | 0.065  | 30.42     | 1.75          | 0.032  | 52.92     | 4.79          | 0.004  | 16.66     | 1.009    |
|              | 446                         | 0.49          | 0.058  | 27.37     | 1.75          | 0.031  | 52.50     | 4.79          | 0.004  | 20.13     | 1.093    |
|              | 456                         | 0.49          | 0.057  | 25.10     | 1.75          | 0.032  | 51.18     | 4.79          | 0.005  | 23.72     | 1.073    |
|              | 466                         | 0.49          | 0.053  | 22.94     | 1.75          | 0.033  | 50.49     | 4.79          | 0.006  | 26.57     | 1.062    |
**Table S2.** Quantum yield (QY) of TPE suspension in a solution of water: THF = 99:1, ZIF-71 powder, TPE@ZIF-71 powder, and pellets.

| Sample                        | QY     |
|-------------------------------|--------|
| TPE suspension in solvent     | 35.64% |
| ZIF-71                        | 3.06%  |
| TPE@ZIF-71                    | 4.12%  |
| Pellet (86.65 MPa)            | 4.49%  |
| Pellet (173.30 MPa)           | 5.87%  |
| Pellet (259.95 MPa)           | 6.08%  |
| Pellet (346.60 MPa)           | 6.35%  |
Table S3. Values of time constants ($\tau_i$), normalized pre-exponential factors ($a_i$), and fractional contributions ($c_i = \tau_i \cdot a_i$) of the emission decay of TPE@ZIF-71 pellets upon excitation at 362.5 nm.

| Pelleting pressure [MPa] | $\lambda_{\text{obs}}$ [nm] | $\tau_1$ [ns] | $a_1$ | $c_1$ [%] | $\tau_2$ [ns] | $a_2$ | $c_2$ [%] | $\tau_3$ [ns] | $a_3$ | $c_3$ [%] | $\chi^2$ |
|--------------------------|-----------------------------|----------------|--------|-----------|----------------|--------|-----------|----------------|--------|-----------|--------|
| 86.65                    | 430                         | 0.54           | 0.062  | 30.69     | 1.92           | 0.029  | 50.79     | 5.64           | 0.004  | 18.52     | 1.057  |
|                          | 440                         | 0.54           | 0.057  | 27.08     | 1.92           | 0.030  | 50.41     | 5.64           | 0.005  | 22.51     | 1.103  |
|                          | 450                         | 0.54           | 0.052  | 24.33     | 1.92           | 0.029  | 47.76     | 5.64           | 0.006  | 27.91     | 1.082  |
|                          | 460                         | 0.54           | 0.050  | 21.33     | 1.92           | 0.029  | 44.90     | 5.64           | 0.008  | 33.77     | 1.062  |
|                          | 470                         | 0.54           | 0.047  | 19.24     | 1.92           | 0.029  | 41.33     | 5.64           | 0.009  | 39.43     | 1.230  |
| 173.30                   | 440                         | 0.56           | 0.050  | 21.48     | 2.23           | 0.029  | 49.93     | 5.75           | 0.006  | 28.58     | 1.137  |
|                          | 450                         | 0.56           | 0.046  | 18.43     | 2.23           | 0.029  | 46.48     | 5.75           | 0.009  | 35.09     | 1.054  |
|                          | 460                         | 0.56           | 0.042  | 16.07     | 2.23           | 0.028  | 42.37     | 5.75           | 0.011  | 41.56     | 1.135  |
|                          | 470                         | 0.56           | 0.040  | 14.10     | 2.23           | 0.027  | 38.43     | 5.75           | 0.013  | 47.48     | 1.118  |
|                          | 480                         | 0.56           | 0.037  | 12.46     | 2.23           | 0.026  | 34.53     | 5.75           | 0.015  | 53.00     | 1.211  |
| 259.95                   | 445                         | 0.57           | 0.043  | 17.34     | 2.24           | 0.031  | 48.97     | 5.77           | 0.008  | 33.69     | 1.157  |
|                          | 455                         | 0.57           | 0.037  | 14.21     | 2.24           | 0.030  | 45.72     | 5.77           | 0.010  | 40.07     | 1.159  |
|                          | 465                         | 0.57           | 0.034  | 12.36     | 2.24           | 0.029  | 41.88     | 5.77           | 0.013  | 45.76     | 1.091  |
|                          | 475                         | 0.57           | 0.032  | 11.06     | 2.24           | 0.027  | 37.06     | 5.77           | 0.015  | 51.87     | 1.165  |
|                          | 485                         | 0.57           | 0.031  | 10.07     | 2.24           | 0.026  | 33.16     | 5.77           | 0.017  | 56.77     | 1.029  |
| 346.60                   | 451                         | 0.59           | 0.040  | 15.59     | 2.27           | 0.031  | 47.52     | 5.81           | 0.010  | 36.90     | 1.096  |
|                          | 461                         | 0.59           | 0.034  | 13.03     | 2.27           | 0.030  | 44.04     | 5.81           | 0.011  | 42.93     | 1.078  |
|                          | 471                         | 0.59           | 0.032  | 11.76     | 2.27           | 0.028  | 40.00     | 5.81           | 0.013  | 48.24     | 1.143  |
|                          | 481                         | 0.59           | 0.030  | 10.35     | 2.27           | 0.027  | 35.85     | 5.81           | 0.016  | 53.80     | 1.091  |
|                          | 491                         | 0.59           | 0.028  | 9.31      | 2.27           | 0.026  | 32.85     | 5.81           | 0.018  | 57.84     | 1.187  |
Table S4. A comparison of the sensitivity of pure TPE versus TPE@ZIF-71. Note: when observed at the same peak wavelength, TPE@ZIF-71 only requires a nominal pressure of ~347 MPa, which is one-tenth of the pressure required for TPE at matching wavelength.

| Sample       | Pressure [MPa] | Peak Wavelength [nm] |
|--------------|----------------|----------------------|
| TPE          | 3500           | 472[1]               |
| TPE@ZIF-71   | 346.6          | 471                  |
References

[1] H. Yuan, K. Wang, K. Yang, B. Liu, and B. Zou, Luminescence properties of compressed tetraphenylethene: the role of intermolecular interactions, J. Phys. Chem. Lett. 17 (2014) 2968-2973.