Supporting Information

for

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

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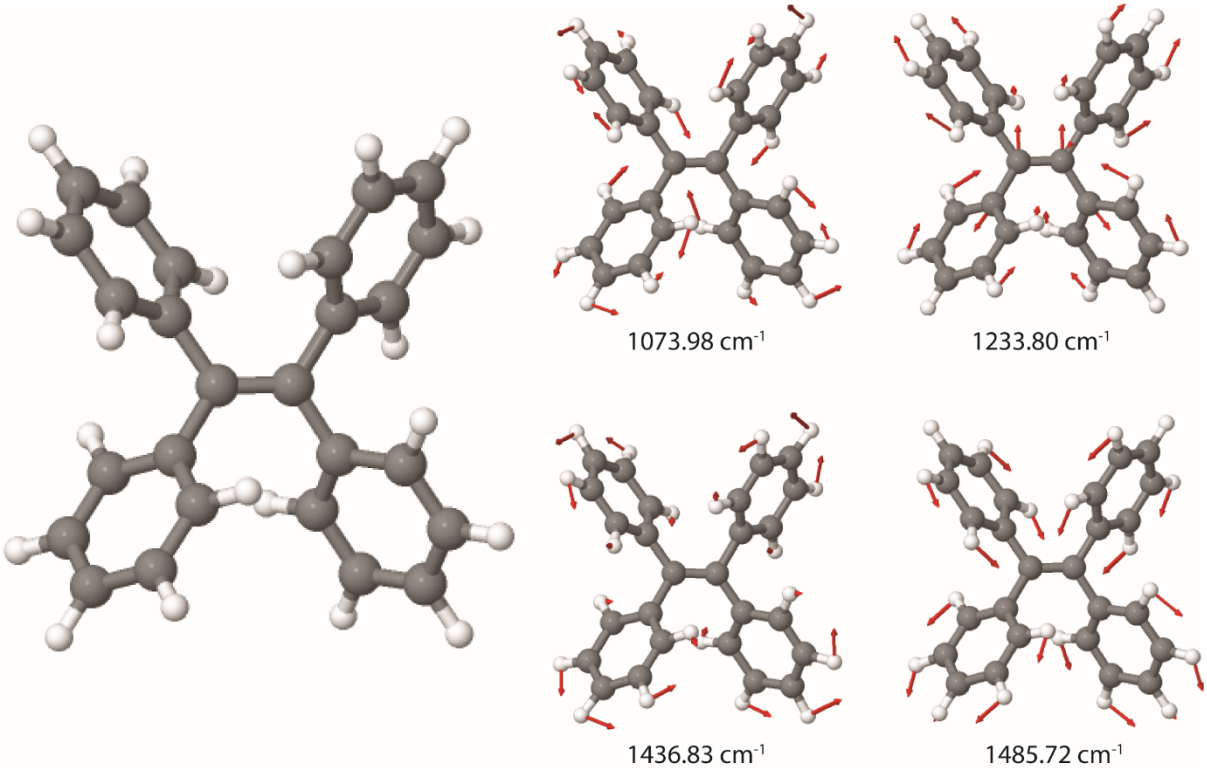

Figure S1. DFT simulation results of TPE monomer and its vibrations at 1073.98 cm^{-1}, 1233.80 cm^{-1}, 1436.83 cm^{-1}, and 1485.72 cm^{-1}. The infrared vibrational frequencies are obtained at the B3LYP/6-311G* level of theory and implementing an empirical scaling factor of 0.97.

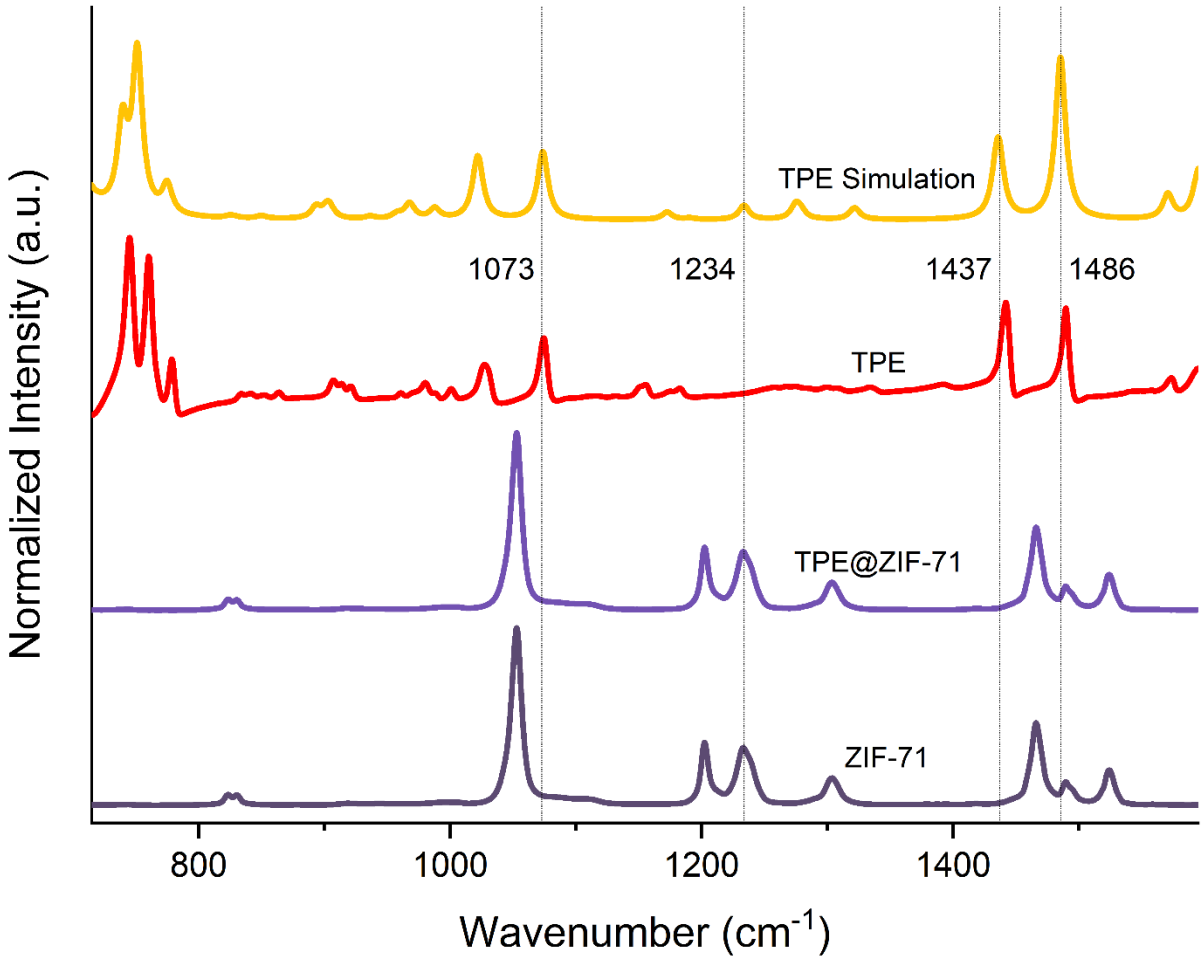

Figure S2. ATR-FTIR spectra of TPE, TPE@ZIF-71 and ZIF-71. The predicted TPE spectrum was obtained from DFT calculations at the B3LYP/6-311G* level of theory and implementing an empirical scaling factor of 0.97.

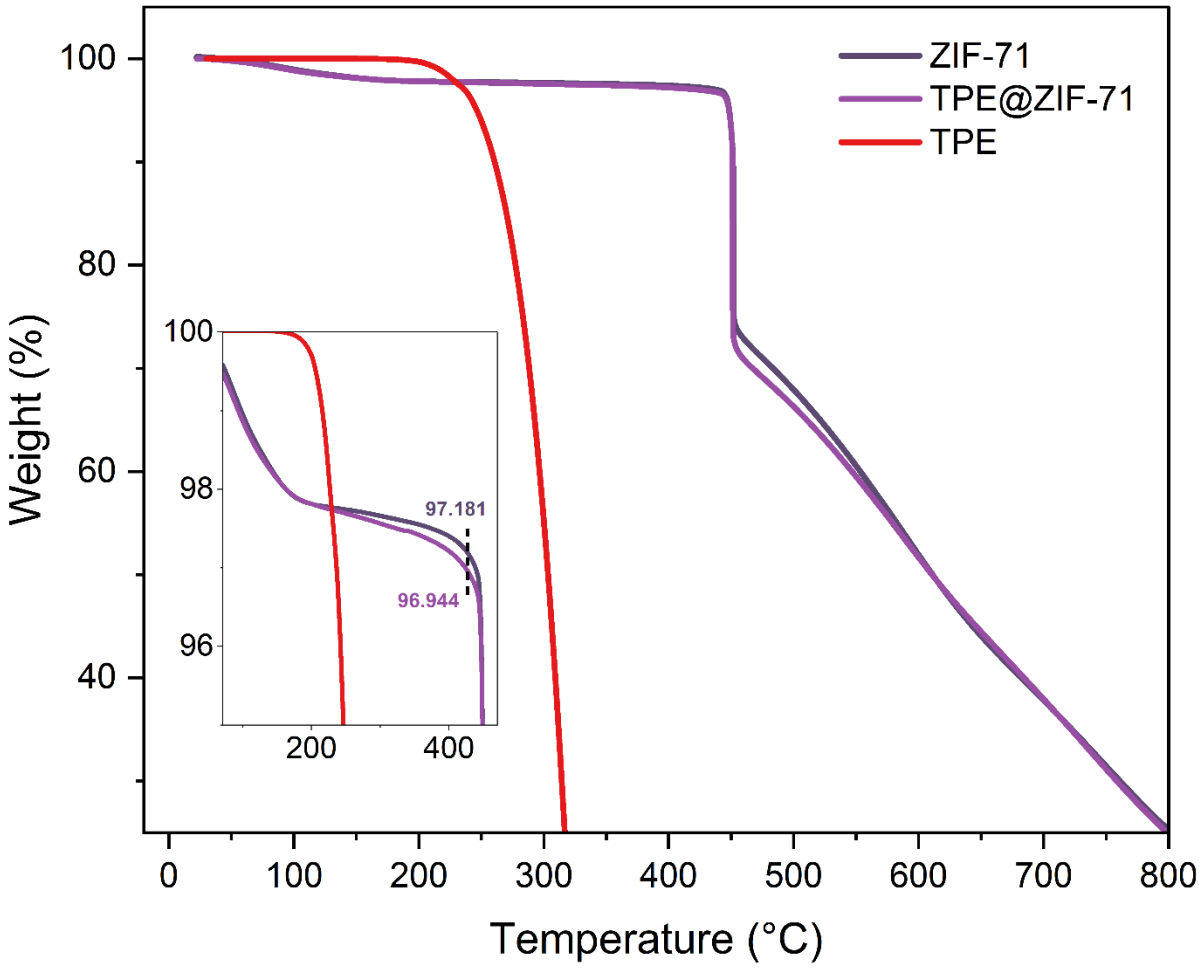

Figure S3. TGA results of TPE, TPE@ZIF-71 and ZIF-71. The wt.% of TPE : ZIF-71 = (97.181 – 96.944) : 96.944 = 0.237 : 96.944

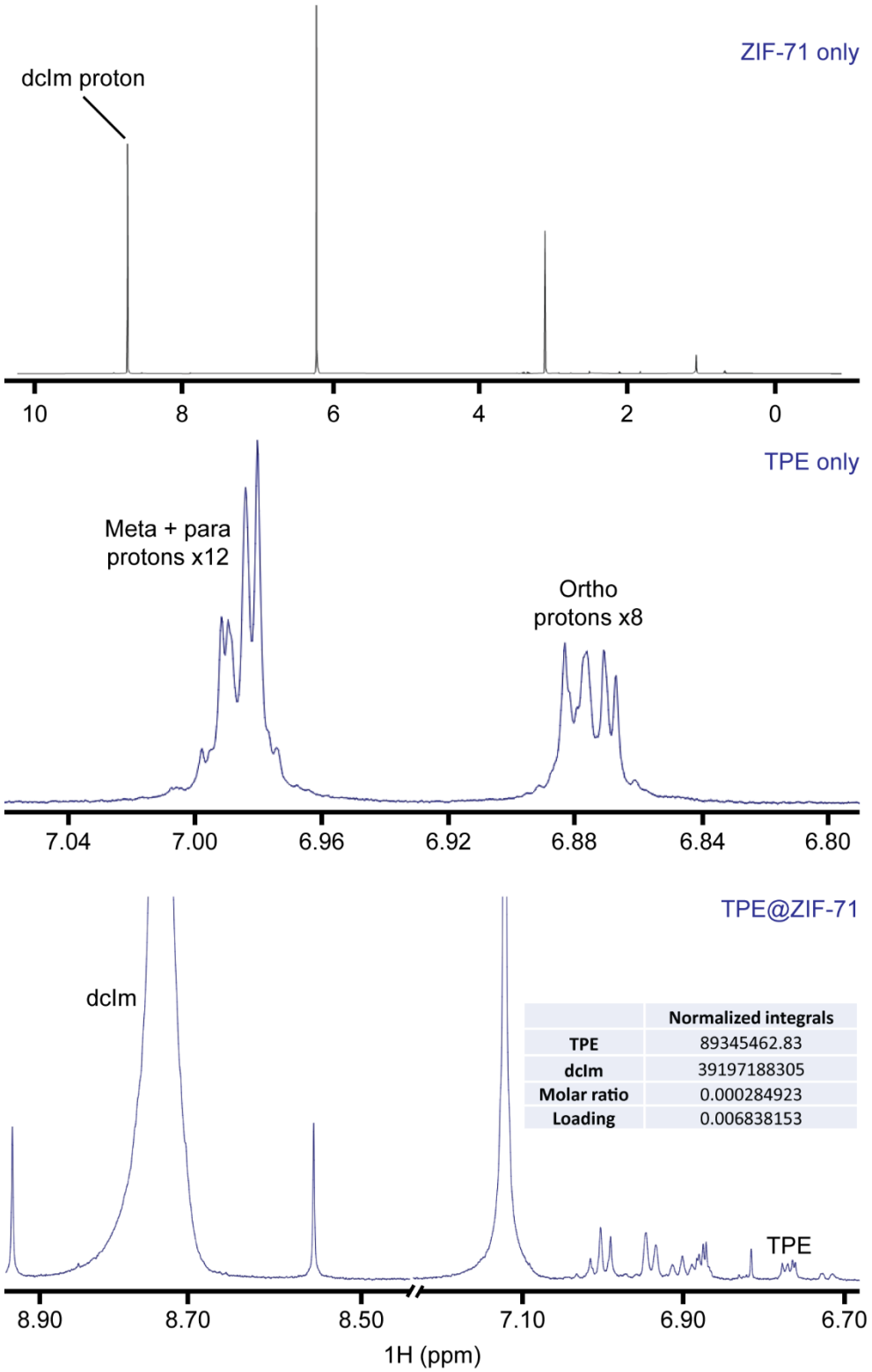

Figure S4. Solution ^{1}H NMR of TPE@ZIF-71 where the guest/host peaks used for integration are indicated as TPE and dcIm, respectively. The guest loading calculated is 1 TPE for every 146 cages of ZIF-71.

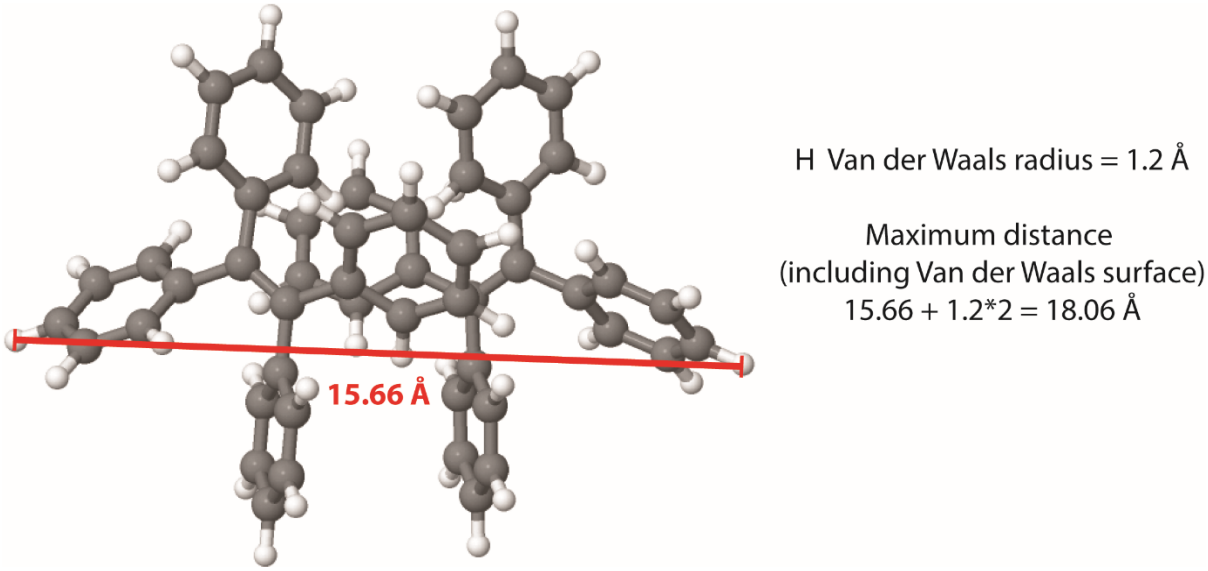

Figure S5. The configuration of the TPE dimer calculated from DFT simulation and its maximum molecular size. The structure is obtained at the B3LYP-D3/6-311G* level of theory.

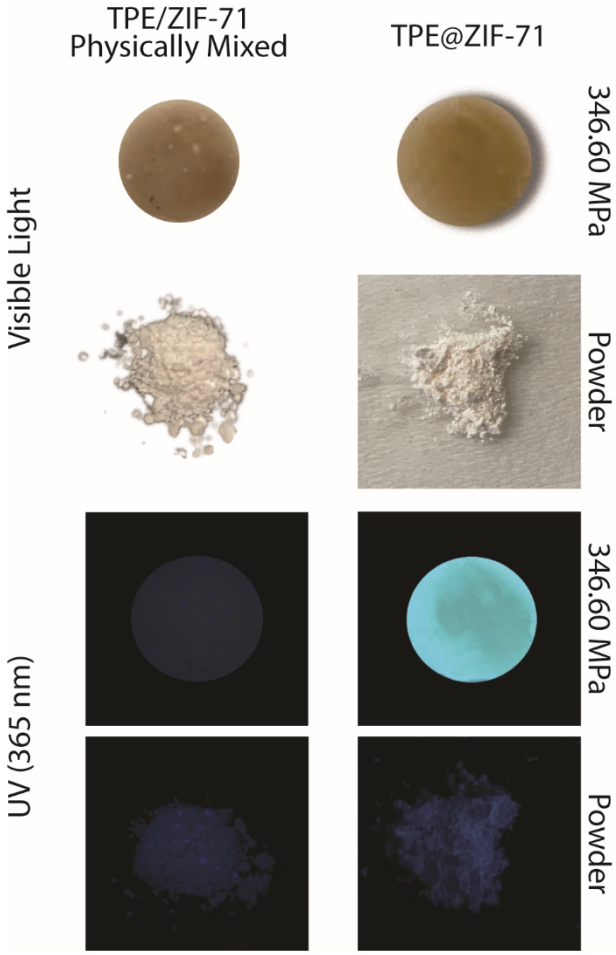

Figure S6. TPE/ZIF-71 pellet prepared using a physically-mixed powder of TPE and ZIF-71, and TPE@ZIF-71 pellet prepared under a nominal pressure of 346.6 MPa, their colors viewed in ambient light, and their fluorescence observed under a 365-nm UV lamp. The wt.% of TPE and ZIF-71 used to prepare the physically-mixed 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.

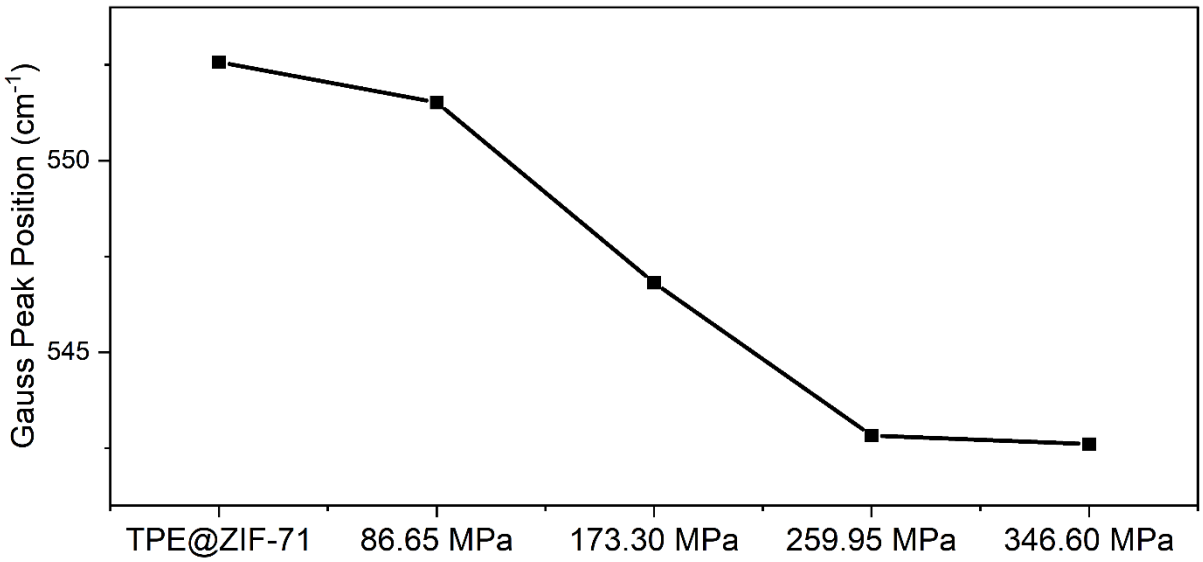

Figure S7. Peak positions of TPE@ZIF-71 and its pellets in the region of 490 – 590 cm^{-1}, as determined from Gauss fittings (in OriginPro).

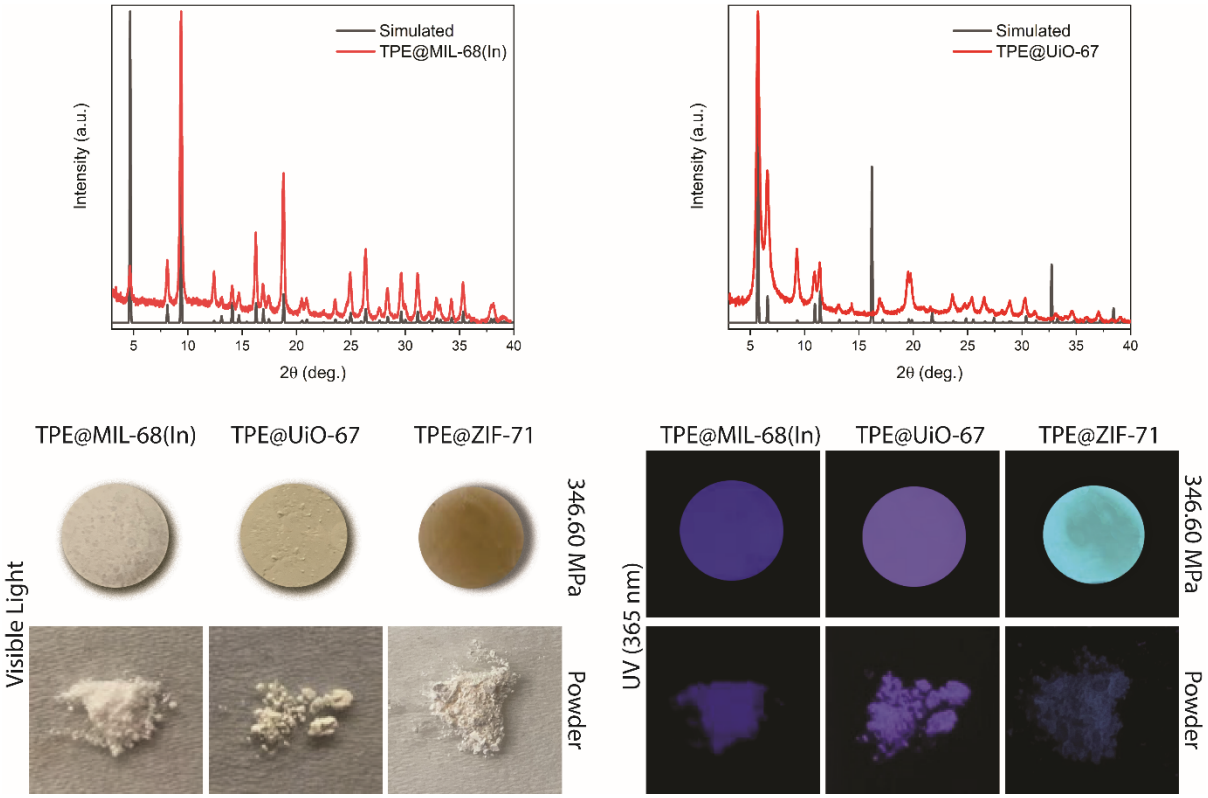

Figure S8. Upper row: XRD patterns of TPE@MIL-68(In) and TPE@UiO-67; Lower row: TPE@MIL-68(In), TPE@UiO-67, and TPE@ZIF-71 pellets prepared under a nominal pressure of 346.6 MPa, their colors viewed in visible light (left), and their fluorescence under a 365 nm UV lamp (right).

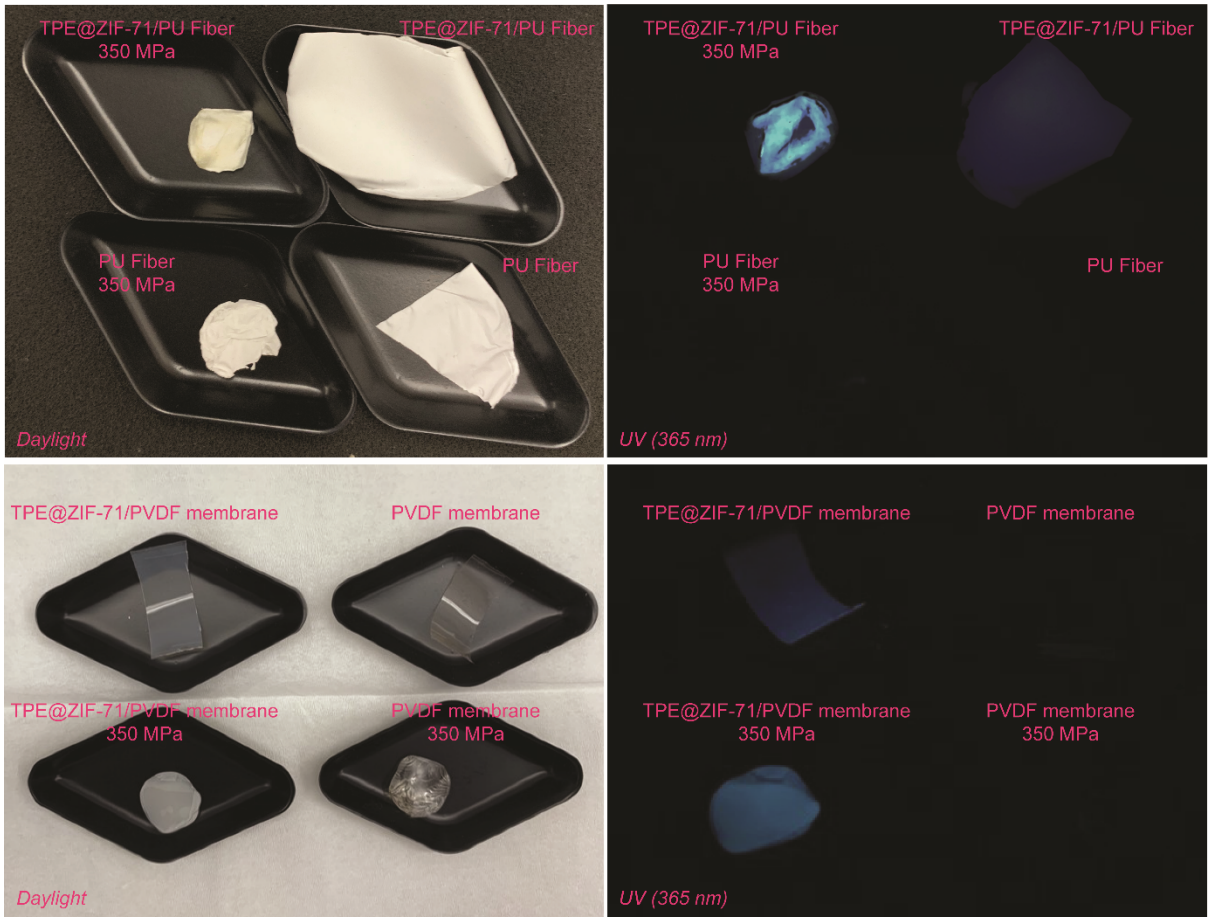

Figure S9. Turn-on type mechanofluorochromic behavior of TPE@ZIF-71/PU fibers and TPE@ZIF-71/PVDF membranes. Note: the samples here are to demonstrate its sensing properties and engineering application potential. More rigorous research will be conducted as follow-on studies.

Table S1. Values of time constants (τ_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	λ_{obs} [nm]	τ_1 [ns]	a_1	c_1 [%]	τ_2 [ns]	a_2	c_2 [%]	τ_3 [ns]	a_3	c_3 [%]	χ^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 (τ_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]	λ_{obs} [nm]	τ_1 [ns]	a_1	c_1 [%]	τ_2 [ns]	a_2	c_2 [%]	τ_3 [ns]	a_3	c_3 [%]	χ^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.