

Electronic Supplementary Information
for

Supramolecular colorimetric pressure sensing: ratiometric quantification based on pressure-modulated association

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Experimental Section

Materials. All commercial reagents and solvents were used as received without further purification. Sample solutions were dissolved in a spectroscopic-grade solvent. The target material (**1**_{PF6}) was synthesized as reported previously.¹

Instruments. The UV/vis/NIR spectra were acquired using a JASCO V-770 spectrometer.

Hydrostatic pressure spectroscopy. Spectroscopic measurements under hydrostatic pressure were performed using a custom-built high-pressure apparatus as described in detail in our previous publication.² In this set-up (Fig. S1), a quartz inner cell (path length of 2 mm) equipped with a Teflon tube was filled with the sample solution. The inner cell was placed within an outer cell containing water, which was hydrostatically pressurized using a hand pump. The entire assembly was mounted in the spectrometers, allowing hydrostatic pressure spectroscopy to be carried out through sapphire windows in the pressure range of 0.1–400 MPa.

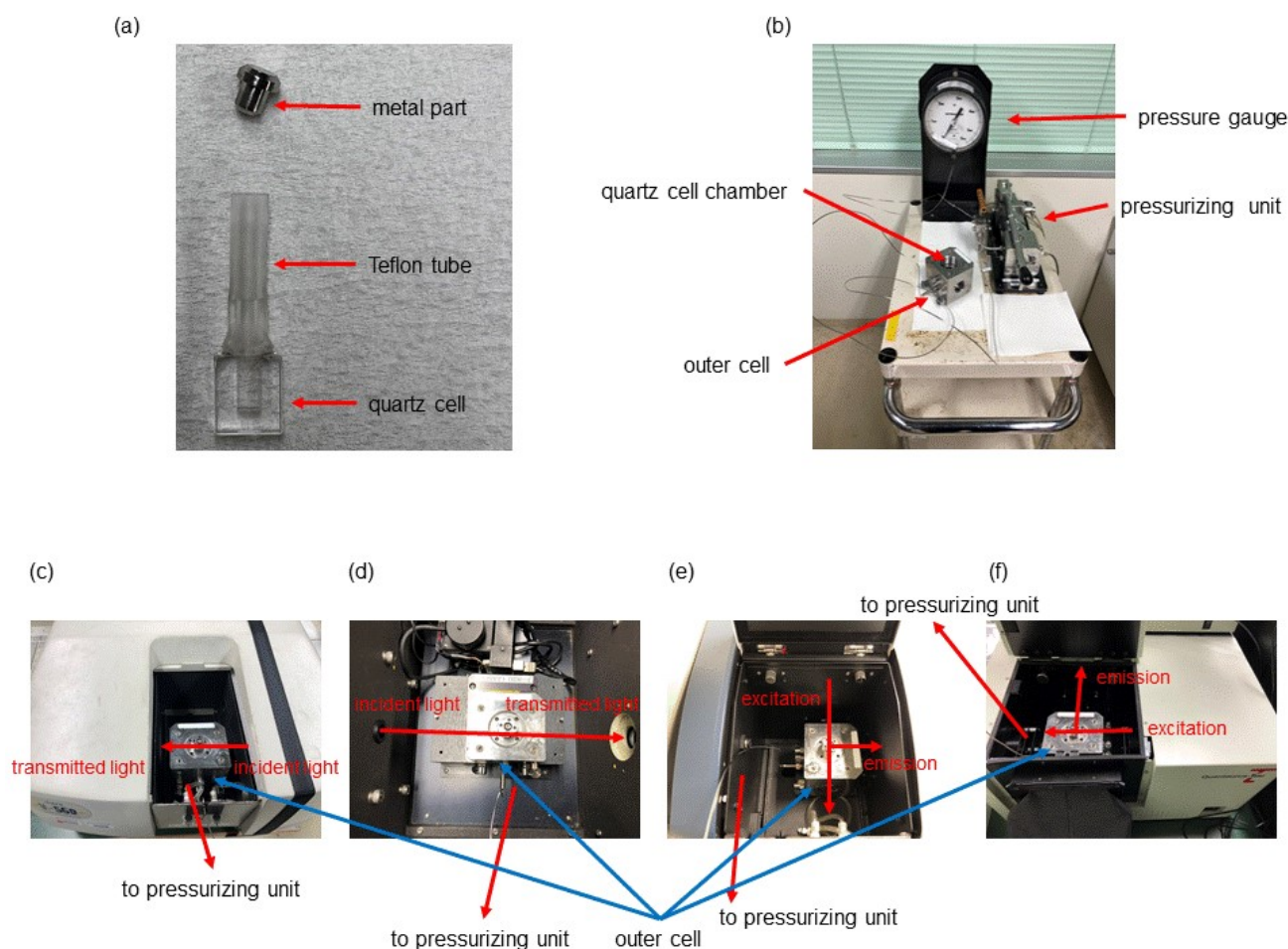


Fig. S1 Photographs of (a) inner quartz cell, (b) pressurizing unit, and setups for (c) UV/vis, (d) circular dichroism, (e) fluorescence, and (f) lifetime measurements. Reproduced with permission from Ref. 2. Copyright 2020 John Wiley & Sons.

¹ M. Murai, M. Abe, S. Ogi and S. Yamaguchi, *J. Am. Chem. Soc.*, 2022, **144**, 20385–20393.

² H. Mizuno, M. Kitamatsu, Y. Imai and G. Fukuhara, *ChemPhotoChem*, 2020, **4**, 502–507.

Structure optimization. All quantum chemical calculations were performed using the Gaussian 16 Revision B.01 program suite.³ Geometry optimizations and property calculations were performed at the M06/6-311+G(d,p) level of theory with solvent effects included using a polarizable continuum model (PCM) for CH₂Cl₂. The optimized geometry of **1PF₆** was confirmed to be at the minimum on the potential energy surface using vibrational frequency analysis which showed no imaginary frequencies. The initial coordinates for a dimer of **1PF₆** were taken from the crystal packing structure. The Cartesian coordinates used in the calculations are listed in Tables S1 and S2.

³ S1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, Jr. J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16, Revision B.01; Gaussian Inc. Wallingford, CT, 2016.

Sample preparation. Spectroscopic measurements of $\mathbf{1_{PF6}}$ in mixed 1,2-dichloroethane (DCE) and methylcyclohexane (MCH) were performed using the samples prepared as follows. First, a solution of $\mathbf{1_{PF6}}$ in DCE was prepared in a vial and another vial containing MCH was prepared. A DCE solution of $\mathbf{1_{PF6}}$ was then slowly injected into the bottom of the vial containing MCH to form separate layers. Subsequently, the vial was inverted thrice to mix the solvents. The resulting solution was then transferred to a high-pressure cell and spectroscopic measurements were performed as quickly as possible.

Calculation of the equilibrium constant K_{dim} for the monomer-dimer equilibrium of $\mathbf{1}_{PF6}$. In the present study, the monomer-dimer equilibrium of $\mathbf{1}_{PF6}$ was assumed to be the primary factor responsible for the observed changes in the absorption spectra. The absorption maximum of $\mathbf{1}_{PF6}$ observed in the DCE/MCH mixed solvent (approximately 800 nm) was close to that observed for crystalline $\mathbf{1}_{PF6}$,⁴ suggesting that similar associated species were formed in both states. Furthermore, crystal structure analysis revealed that the two nearest-neighbor molecules formed a closely associated dimer, whereas the spatial separation between individual dimers was somewhat larger, indicating that the inter-dimer interactions were relatively weak. Based on these observations, the absorption peak at approximately 800 nm is considered to originate predominantly from the dimer species, even though higher-order aggregates may be present in the solution. Accordingly, the absorption behavior of the present system is assumed to be approximately described in terms of the monomer-dimer equilibrium, and the discussion in this study is based on this assumption.

Based on this assumption, in the following fitting analysis, $\mathbf{1}_{PF6}$ was assumed to exist as a monomer in DCE solution (Fig. 2a in the main text), whereas it exists mainly as a dimer in the DCE/MCH = 1/9 (v/v) mixed solvent (Fig. S2). Because the absorption spectrum of the dimer overlaps that of the monomer in mixed solvents, the contribution of the dimer absorption peak (at approximately 800 nm) to the apparent monomer absorption peak (at approximately 650 nm) was estimated using the spectrum measured in the DCE/MCH = 1/9 solution. From the averaged absorption spectra at each pressure of $\mathbf{1}_{PF6}$ in the DCE/MCH = 1/9 (v/v) mixed solvent, the ratio ($R_{M/D}$) of the monomer absorption intensity (I_{650}) of the peak at approximately 650 nm to the dimer absorption intensity (I_{800}) of the peak at approximately 800 nm was determined using Equation S1.

$$R_{M/D} = \frac{I_{650}}{I_{800}} \#(S1)$$

The actual monomer absorption intensity (I_M) was calculated from the apparent monomer absorption intensity ($I_{M,app}$) and the dimer absorption intensity (I_D) for each mixed solvent composition according to Equation S2:

$$I_M = I_{M,app} - R_{M/D}I_D \#(S2)$$

The concentration of the monomer (C_M) was determined using the molar absorption coefficient of $\mathbf{1}_{PF6}$ in the DCE solution (Figure S2), whereas the concentration of the dimer (C_D) was calculated from the prepared concentration (C_0) according to Equation S3.

$$C_D = \frac{C_0 - C_M}{2} \#(S3)$$

Finally, the equilibrium constant was calculated using equation S4.

$$K_{dim} = \frac{C_D}{C_M^2} \#(S4)$$

⁴ M. Murai, M. Abe, S. Ogi and S. Yamaguchi, *J. Am. Chem. Soc.*, 2022, **144**, 20385–20393.

Absorption of 1_{PF6} dimer

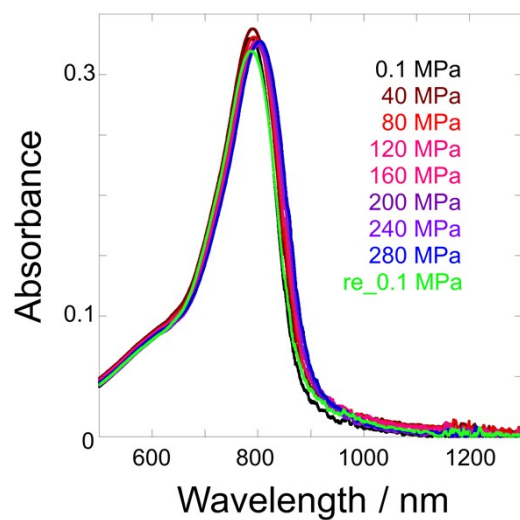


Figure S2. UV/vis spectra of 1_{PF6} in DCE/MCH = 1/9 (v/v) (50 μ M) at 0.1, 40, 80, 120, 160, 200, 240, and 280 MPa (from black to blue) at room temperature, measured in a high-pressure cell. The green line indicates the spectrum obtained at 0.1 MPa after depressurization from 280 MPa.

Full absorption spectra of 1_{PF6} .

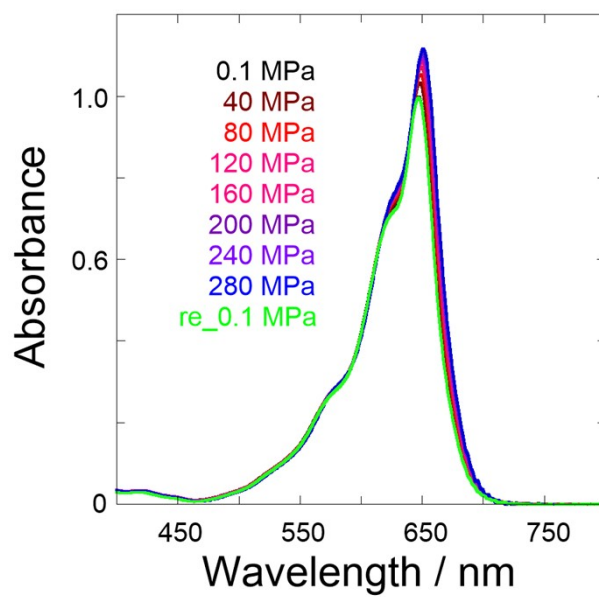


Figure S3. Full absorption spectra of 1_{PF6} in DCE (39 μM) at 0.1, 40, 80, 120, 160, 200, 240, and 280 MPa (from black to blue) at room temperature, measured in a high-pressure cell. The green line indicates the spectrum at 0.1 MPa after depressurization from 280 MPa.

Expanded views of the absorption peak maxima of 1_{PF6} .

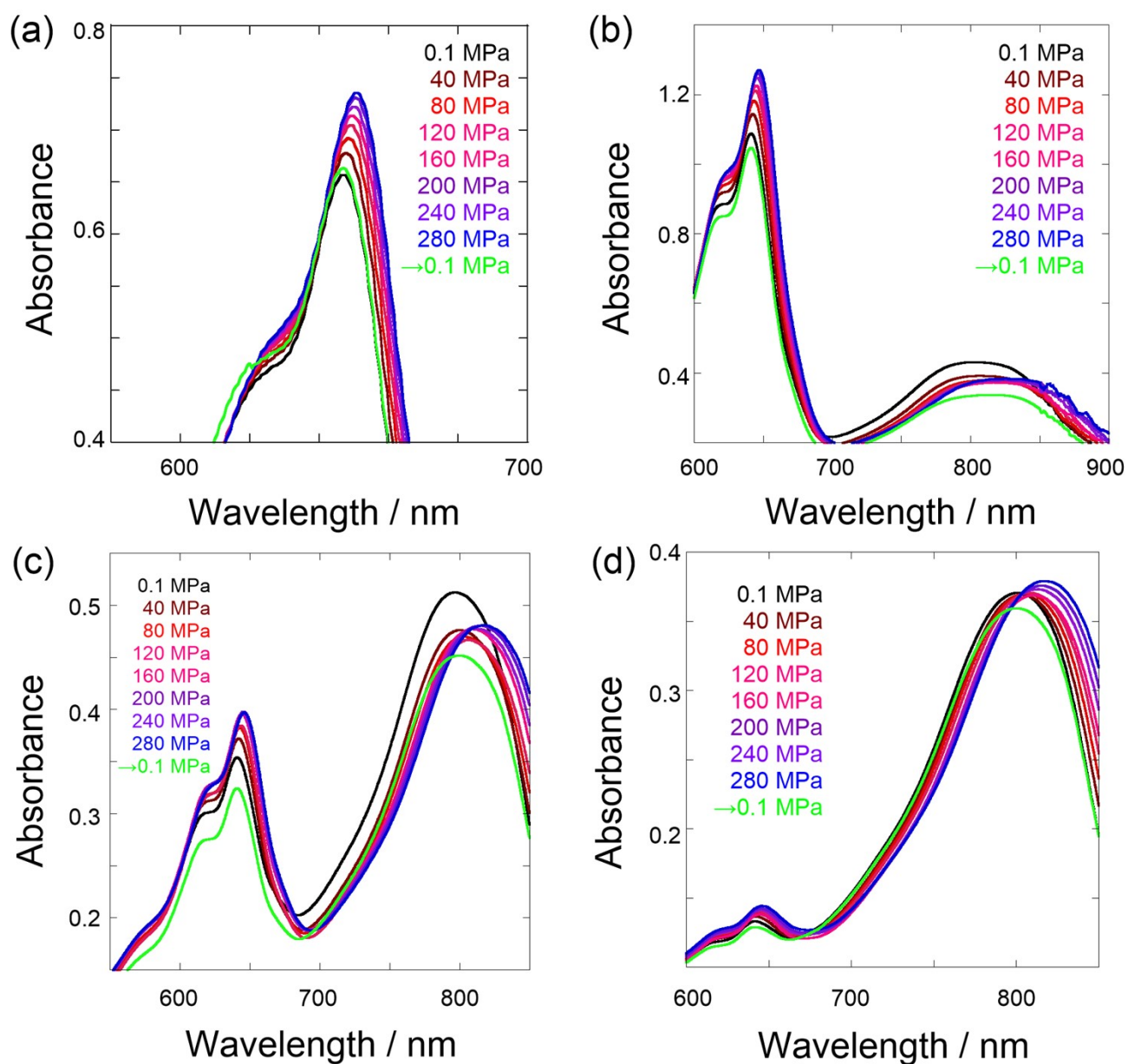


Figure S4. Expanded views of the absorption peak maxima of 1_{PF6} in (a) DCE (39 μ M), (b) DCE/MCH = 4/6 (v/v) (200 μ M), (c) DCE/MCH = 3/7 (v/v) (100 μ M), and (d) DCE/MCH = 2/8 (v/v) (50 μ M) at 0.1, 40, 80, 120, 160, 200, 240, and 280 MPa (from black to blue) at room temperature, measured in a high-pressure cell. The green line indicates the spectrum at 0.1 MPa after depressurization from 280 MPa.

Reproducibility measurements for determining the pressure-dependent K_{dim}

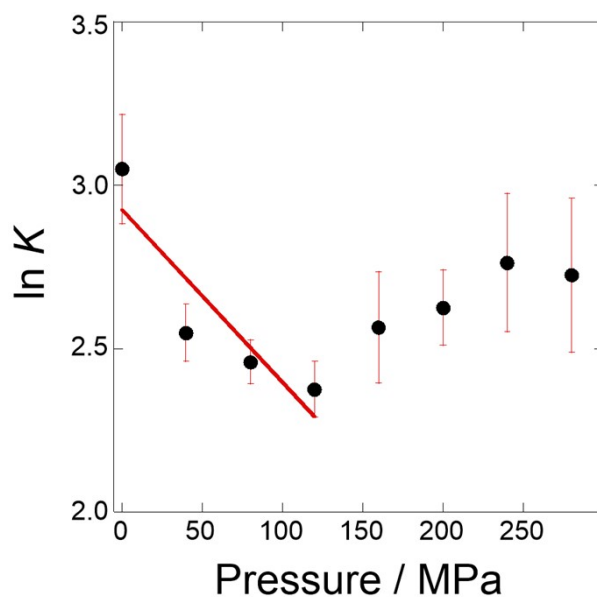


Figure S5. Pressure dependence of K_{dim} for the monomer-dimer equilibrium of $\mathbf{1}_{\text{PF}_6}$ in DCE/MCH = 2/8 (v/v) (50 μM) at 0.1, 40, 80, 120, 160, 200, 240, and 280 MPa at room temperature, measured in a high-pressure cell, with mean values and standard errors obtained from three independent measurements (Fig. 2a, S6, and S7).

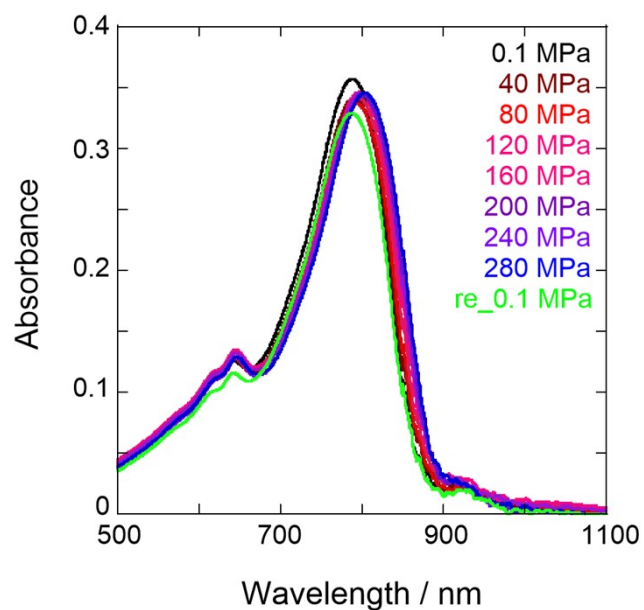


Figure S6. UV/vis/NIR absorption spectra of 1_{PF6} in DCE/MCH = 2/8 (v/v) (50 μM) at 0.1, 40, 80, 120, 160, 200, 240, and 280 MPa (from black to blue) at room temperature, measured in a high-pressure cell. The green line indicates the spectrum at 0.1 MPa depressurized from 280 MPa (run2).

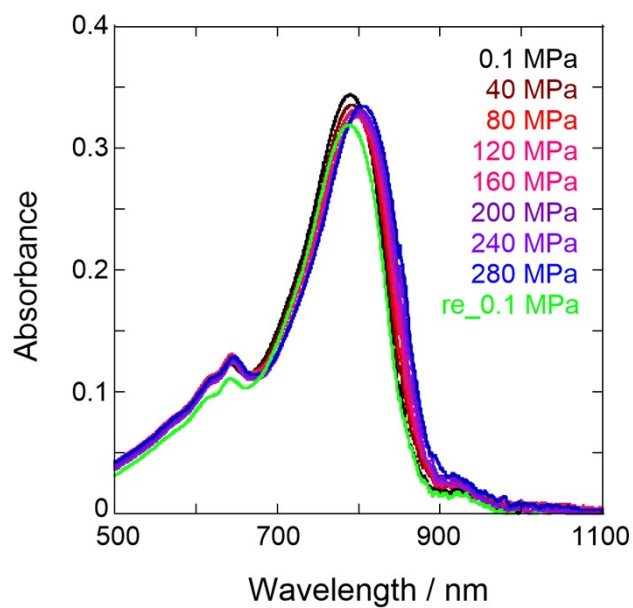


Figure S7. UV/vis/NIR absorption spectra of 1_{PF6} in DCE/MCH = 2/8 (v/v) (50 μ M) at 0.1, 40, 80, 120, 160, 200, 240, and 280 MPa (from black to blue) at room temperature, measured in a high-pressure cell. The green line indicates the spectrum at 0.1 MPa depressurized from 280 MPa (run3).

Pressure dependence of the frequencies of absorption maxima

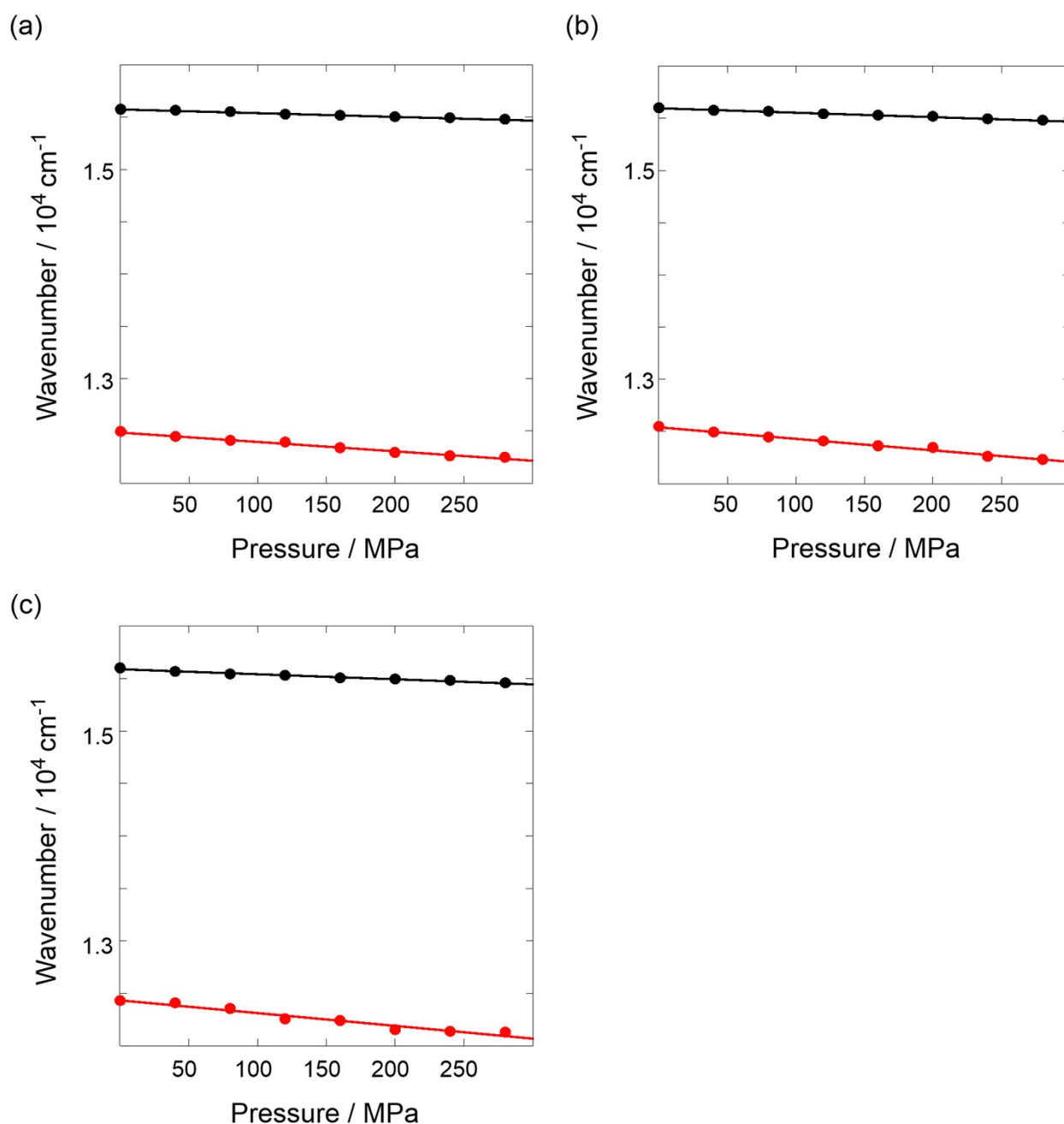


Figure S8. Plots of the frequencies of absorption maxima of 1_{PF_6} at different pressures in (a) DCE/MCH = 2/8 (v/v) (50 μM), (b) DCE/MCH = 3/7 (v/v) (100 μM), and (c) DCE/MCH = 4/6 (v/v) (200 μM). Regression lines for the monomer and dimer are shown by black lines ((a) slope = $-0.355 \text{ cm}^{-1} \text{ MPa}^{-1}$, $r = 0.995$, (b) slope = $-0.424 \text{ cm}^{-1} \text{ MPa}^{-1}$, $r = 0.996$, and (c) slope = $-0.477 \text{ cm}^{-1} \text{ MPa}^{-1}$, $r = 0.988$) and red lines ((a) slope = $-0.901 \text{ cm}^{-1} \text{ MPa}^{-1}$, $r = 0.993$, (b) slope = $-1.10 \text{ cm}^{-1} \text{ MPa}^{-1}$, $r = 0.994$, and (c) slope = $-1.22 \text{ cm}^{-1} \text{ MPa}^{-1}$, $r = 0.977$), respectively.

Table S1. Cartesian coordinates (Å) of the optimized structure of 1_{PF6} monomer calculated by DFT at the M06/6-311+G(d,p) level of theory with PCM (CH₂Cl₂).

Label	Element	x	y	Z	Label	Element	x	y	z
1	C	2.322336	3.299974	0.140517	38	H	5.853646	0.245781	-1.04197
2	H	3.164814	3.959407	0.322326	39	C	4.609354	0.899479	1.924892
3	C	2.360584	1.926015	0.068279	40	H	5.402337	0.151957	2.036912
4	C	1.02544	1.45344	-0.18279	41	H	3.88253	0.754533	2.729093
5	C	0.15591	2.591497	-0.26601	42	H	5.059551	1.891502	2.040503
6	C	-1.20763	2.552835	-0.50441	43	Si	3.806039	0.744086	0.247222
7	H	-1.6444	1.568783	-0.66137	44	P	-3.59347	-0.68789	0.279737
8	C	-2.10288	3.61457	-0.57565	45	F	-2.34285	-0.41342	1.288982
9	H	-3.13672	3.336172	-0.76058	46	F	-4.81393	-0.9574	-0.75182
10	C	-1.85718	4.974493	-0.43999	47	F	-3.25672	-2.27984	0.302849
11	H	-2.72985	5.615953	-0.53622	48	F	-2.56531	-0.50638	-0.99222
12	C	-0.6567	5.636405	-0.20101	49	F	-3.90261	0.908644	0.234829
13	H	-0.72015	6.719404	-0.13866	50	F	-4.59203	-0.86344	1.540773
14	C	0.608876	5.095785	-0.03116					
15	H	1.414318	5.806733	0.146363					
16	C	0.990019	3.760396	-0.05314					
17	C	3.41044	-2.18378	0.124231					
18	H	4.442896	-2.4722	0.293163					
19	C	2.920233	-0.89899	0.063589					
20	C	1.504022	-0.97077	-0.17623					
21	C	1.132709	-2.35393	-0.25567					
22	C	-0.14763	-2.83883	-0.4633					
23	H	-0.93618	-2.09953	-0.5861					
24	C	-0.57025	-4.16181	-0.53297					
25	H	-1.63671	-4.29788	-0.69079					
26	C	0.179804	-5.32546	-0.42681					
27	H	-0.38313	-6.25111	-0.51947					
28	C	1.546763	-5.47933	-0.21756					
29	H	1.904219	-6.50454	-0.17231					
30	C	2.511615	-4.49686	-0.05437					
31	H	3.53036	-4.8471	0.104514					
32	C	2.353028	-3.11699	-0.06329					
33	C	0.641872	0.118098	-0.29454					
34	H	-0.41064	-0.09076	-0.47666					
35	C	5.055733	0.992617	-1.1179					
36	H	5.511622	1.985676	-1.04066					
37	H	4.591268	0.901778	-2.10393					

Table S2. Cartesian coordinates (Å) of the structure of 1_{PF6} dimer taken from the crystal packing structure.

Label	Element	x	Y	z	Label	Element	x	y	z
1	Si	4.062756	3.806826	0.137275	38	C	8.885959	1.329105	0.252767
2	C	5.484017	2.601117	0.329462	39	H	9.408571	2.121089	0.212881
3	C	0.660749	1.943799	1.565709	40	C	-1.11166	-0.45837	2.45933
4	C	2.674341	2.758575	0.819991	41	H	-1.81254	-1.0373	2.736115
5	C	5.231186	1.190786	0.534819	42	C	9.114674	-1.16258	0.303128
6	C	6.483543	0.491327	0.494396	43	H	9.77231	-1.84316	0.222363
7	C	2.818697	1.336356	1.000038	44	P	3.608697	-3.45118	-0.79233
8	C	0.096907	-1.0846	2.177781	45	F	3.743555	-1.94808	-1.33239
9	H	0.110936	-2.02634	2.301912	46	F	3.493348	-4.93259	-0.23219
10	C	3.994807	0.613138	0.817192	47	F	5.196187	-3.53438	-0.70635
11	H	3.951299	-0.33343	0.889363	48	F	3.571923	-2.87697	0.686977
12	C	1.559819	0.801067	1.459275	49	F	2.03322	-3.34763	-0.87622
13	C	-0.66423	1.953414	1.987129	50	F	3.678637	-4.00439	-2.27171
14	H	-1.09004	2.802862	1.995895	51	Si	-4.31844	3.838221	-0.41864
15	C	6.847541	2.764657	0.221237	52	C	-2.89958	1.35091	-0.77297
16	H	7.285621	3.598627	0.098079	53	C	-1.62269	0.826206	-1.15898
17	C	7.506119	1.511095	0.317927	54	C	-7.00914	2.627359	-0.19288
18	C	6.646383	-0.87841	0.580568	55	H	-7.49601	3.443068	-0.19012
19	H	5.855067	-1.37994	0.736824	56	C	-5.30039	1.133136	-0.26937
20	C	-1.44478	0.88155	2.397904	57	C	-6.50787	0.374135	-0.12672
21	H	-2.32765	1.098717	2.673159	58	C	-6.58938	-1.00093	-0.06201
22	C	3.740918	4.114343	-1.671	59	H	-5.76702	-1.4694	-0.14398
23	H	4.504255	4.587623	-2.06288	60	C	-2.86392	2.779255	-0.90627
24	H	3.616664	3.257647	-2.13088	61	C	-5.63905	2.530821	-0.29828
25	H	2.932331	4.658777	-1.77101	62	C	-4.02357	0.59808	-0.4483
26	C	1.295051	-0.51513	1.735083	63	H	-3.9152	-0.3397	-0.3422
27	H	2.01881	-1.11753	1.609536	64	C	-1.62208	3.12815	-1.36178
28	C	1.381182	3.096782	1.158589	65	H	-1.33474	4.018242	-1.53078
29	H	1.023272	3.975739	1.125086	66	C	-1.25792	-0.50145	-1.14744
30	C	7.820526	-1.61562	0.469174	67	H	-1.91547	-1.10919	-0.82944
31	H	7.717957	-2.55936	0.513252	68	C	0.48156	1.984405	-2.02854
32	C	4.2296	5.424191	1.011436	69	H	0.844601	2.840369	-2.22157
33	H	3.461259	5.992705	0.795425	70	C	1.311459	0.908117	-2.25956
34	H	4.260328	5.270447	1.979046	71	H	2.166493	1.120067	-2.61366
35	H	5.055092	5.866849	0.724586	72	C	-8.95663	1.092145	0.041165
36	C	9.59768	0.125903	0.237641	73	H	-9.51928	1.857318	0.03061
37	H	10.54174	0.207551	0.174056	74	C	-0.0546	-1.06414	-1.53902

Label	Element	x	y	z
75	H	0.006365	-2.00774	-1.44868
76	C	-7.7184	-1.78424	0.106483
77	H	-7.56438	-2.72043	0.149808
78	C	-7.59131	1.339267	-0.08813
79	C	-0.82536	1.967876	-1.54557
80	C	-9.04335	-1.39019	0.222301
81	H	-9.66607	-2.09637	0.346698
82	C	-9.59186	-0.11892	0.180338
83	H	-10.5377	-0.07826	0.260789
84	C	1.073101	-0.43787	-2.04712
85	H	1.7871	-1.01775	-2.28321
86	C	-3.97638	4.547368	1.261113
87	H	-3.23907	5.189754	1.201185
88	H	-3.73135	3.825208	1.877177
89	H	-4.77896	5.001393	1.593902
90	C	-4.68868	5.128939	-1.67568
91	H	-4.85758	4.702177	-2.542
92	H	-3.92425	5.736798	-1.75499
93	H	-5.48156	5.63482	-1.4011
94	P	-3.34294	-3.69965	0.44101
95	F	-2.96899	-5.08179	-0.25362
96	F	-3.7086	-2.29908	1.128826
97	F	-4.88856	-4.05678	0.360428
98	F	-1.81108	-3.31644	0.501984
99	F	-3.46394	-2.98402	-0.97502
100	F	-3.24968	-4.38292	1.855231