

Supplementary Information

For

Crystal Structures and Properties of a Monoprotonated Porphyrin

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Preparation

Synthesis of **1**: H₂DPP and 2-anthracene sulfonic acid were mixed in toluene. On the green solution of the mixture, methanol was pored slowly to give a two-layered solution. The slow diffusion of the methanol gave green crystals of **1**. Absorption maximum in PhCN (λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)); 485 (1.4×10^5), 725 (1.9×10^4).

Synthesis of **2**: The green crystals of **2** were obtained by using CH₂Cl₂ in place of toluene in the procedure for **1**. Elemental analysis: calcd for **2**•CH₃OH•CH₂Cl₂ (C₂₀₁H₁₄₄N₈O₈S₂Cl₂); C 82.27, H 4.95, N 3.82 %. Found: C 82.29; H 4.83, N 3.89 %. Absorption maximum in PhCN (λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)); 492 (1.5×10^5), 726 (2.4×10^4).

Synthesis of **3**: The green crystals of **3** were obtained by the same method as that for **1** by using 2-anthracene carboxylic acid in place of 2-anthracene sulfonic acid. Elemental analysis: calcd for **3**•CH₃OH•H₂O (C₁₂₄H₉₂N₄O₇); C 85.10, H 5.30, N 3.20 %. Found: C 85.37, H 5.08, N 3.22 %. Absorption maximum in PhCN (λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)); 505 (1.5×10^5), 743 (3.4×10^4).

Details of X-ray crystallography.

For the structure refinements of **1** and **2**, the SQUEEZE program¹ was applied to remove unspecified solvent molecules of crystallization except the hydrogen-bonded methanol molecules. In the data processing for **3**, the HKL2000 program² was applied to use diffractions in the range from 6.79 Å (low) to 1.00 Å (high) in resolution. All structures were solved by direct methods by using the *CrystalStructure* program package (Rigaku Corp.) and SHELX-97.

In the crystal structure of **1**, the occupancy of the two sets of disordered 2-AN-SO₃⁻ anions were set to be 0.5. We set the occupancies of two of the hydrogen-bonded methanol molecules to be 0.5 and could not set the O-H proton of hydrogen-bonded methanol molecule due to the disorder. In the case of **2**, severe disorder of hydrogen-bonded methanol molecule did not allow us to fix all of its hydrogen atoms.

In addition, all the hydrogen atoms of methanol molecule of crystallization could not be set even at calculated positions in the structure of **3**, due to its severe disorder.

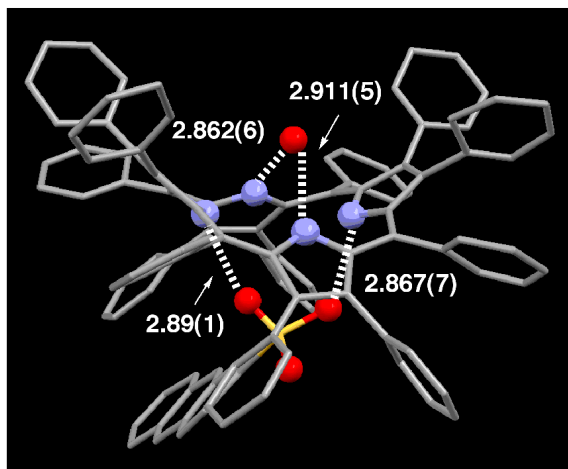
Table S1 Crystallographic data for **1 - 3**.

	1	2	3
formula	C ₁₀₇ H ₇₅ N ₄ O ₄ S	C ₁₀₁ H ₆₈ Cl ₂ N ₄ O ₄ S	C ₁₄₄ H ₁₀₆ N ₄ O ₅
mol weight	1512.77	1504.64	1972.45
crystal system	monoclinic	triclinic	monoclinic
space group	<i>P2₁/a</i> (no. 14)	<i>P-1</i> (no. 2)	<i>P2₁/c</i> (no. 14)
<i>a</i> , Å	15.291(5)	16.024(3)	18.383(1)
<i>b</i> , Å	24.074(9)	16.575(3)	20.782(1)
<i>c</i> , Å	24.824(9)	18.866(4)	29.219(1)
α , deg		74.873(7)	
β , deg	90.017(9)	79.655(8)	103.722(1)
γ , deg		68.318(7)	
<i>V</i> , Å ³	9138(6)	4475.6(16)	10844.1(9)
<i>Z</i>	4	2	4
<i>T</i> , K	123	123	123
No of diff measd	85079	18122	11309
No of diff unique	20711	16425	11309
<i>R</i> _{int}	0.0748	0.028	0.054
<i>R</i> 1 (<i>R</i> _w) (<i>I</i> > 2σ(<i>I</i>))	0.1052 (0.2919)	0.0926 (0.2992)	0.0499 (0.1301)
<i>R</i> (<i>R</i> _w) (all data)	0.1560 (0.3302)		
GOF	1.006	0.975	1.039
CCDC number	CCDC-727605	CCDC-727606	CCDC-727607

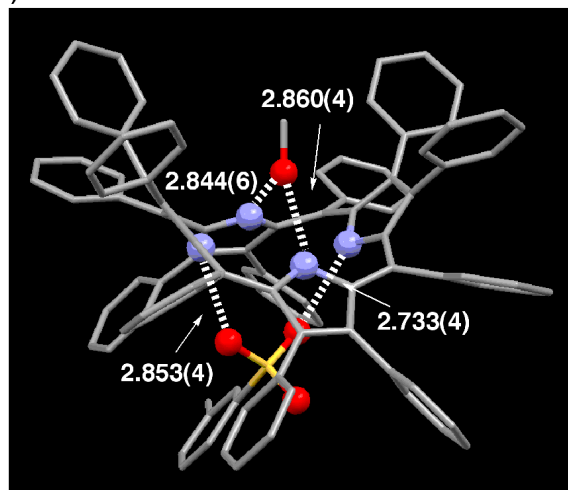
References

1. (a) P. van der Sluis, A. L. Spek, *Acta Crystallogr.*, 1990, **A46**, 194; (b) A. L. Spek, *Acta Crystallogr.*, 1990, **A46**, C34.
2. Z. Otwinowski, W. Minor, in *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology, Volume 276: Macromolecular Crystallography, part A* (Eds.: C. W. Carter, Jr. & R. M. Sweet), Academic Press, New York, 1997, pp. 307-326.

(a)



(b)



(c)

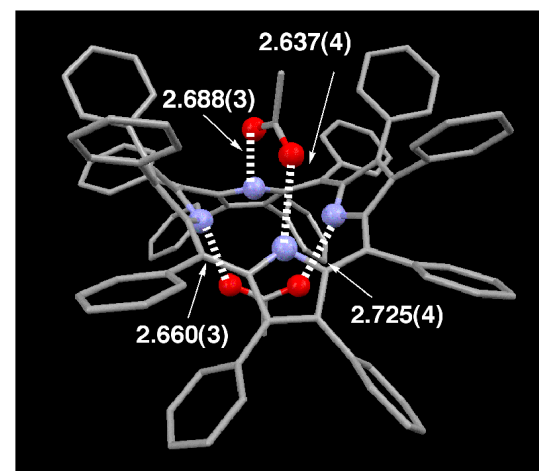


Fig. S1 Interatomic distances of hydrogen bonding in the crystal structures of **1** (a), **2** (b), and **3** (c).

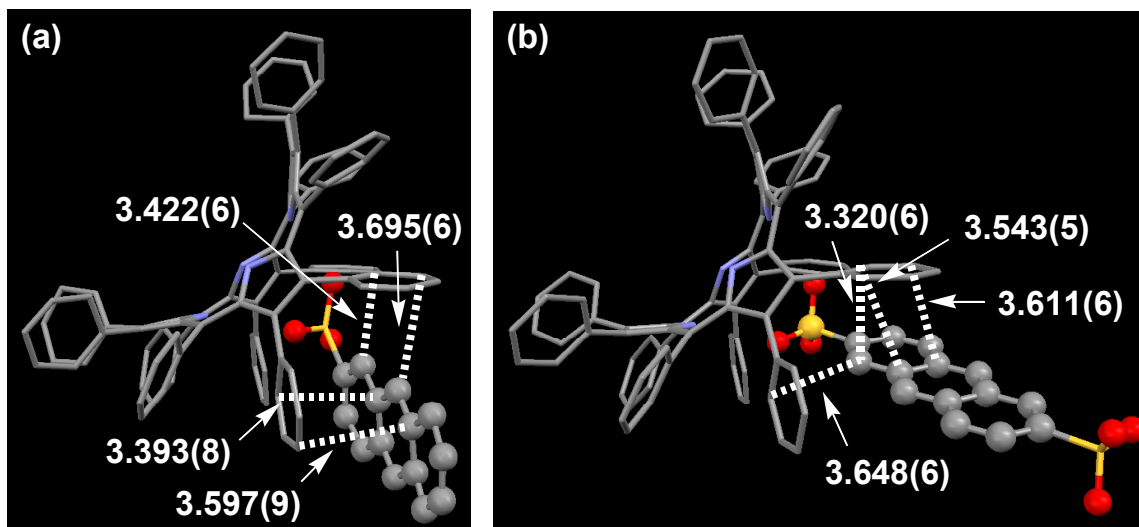


Fig. S2 Intra-supramolecular π - π interactions found in **1** (a) and **2** (b). Values are given in the unit of angstrom. Hydrogen atoms are omitted for clarity.

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Fig. S3 Crystal structures of **3**. Gray carbon, blue nitrogen, red oxygen, Hydrogen atoms and solvent molecules of crystallization are omitted for clarity.

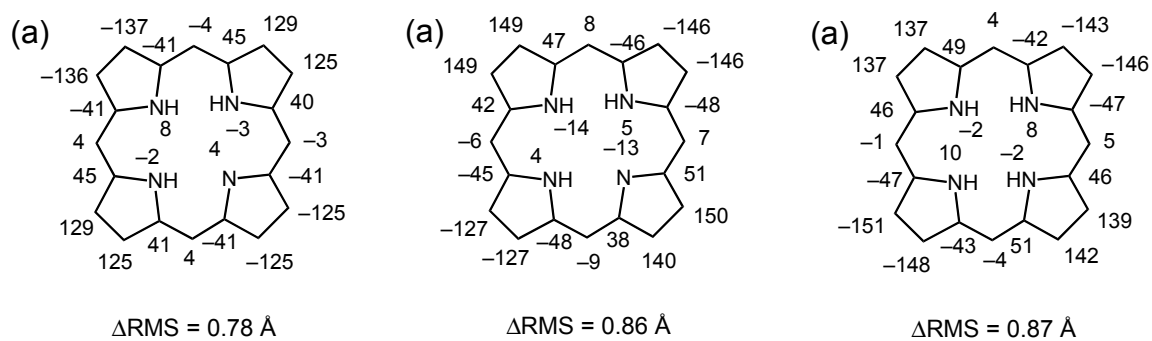
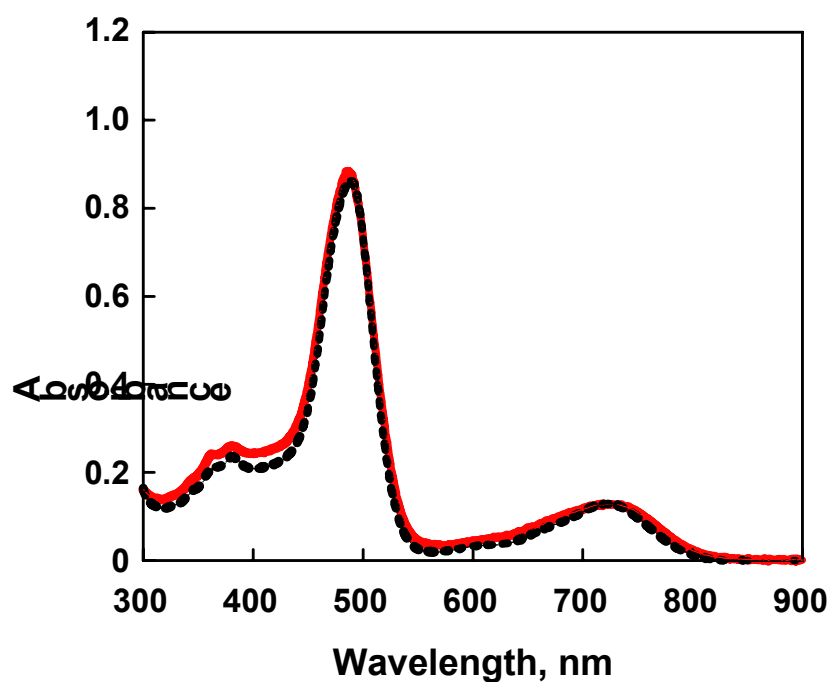


Fig. S4 The displacement of each atom from the least-squares mean plane of porphyrin (in units of 0.01 \AA) in **1** (a), **2** (b) and **3** (c).

(a)



(b)

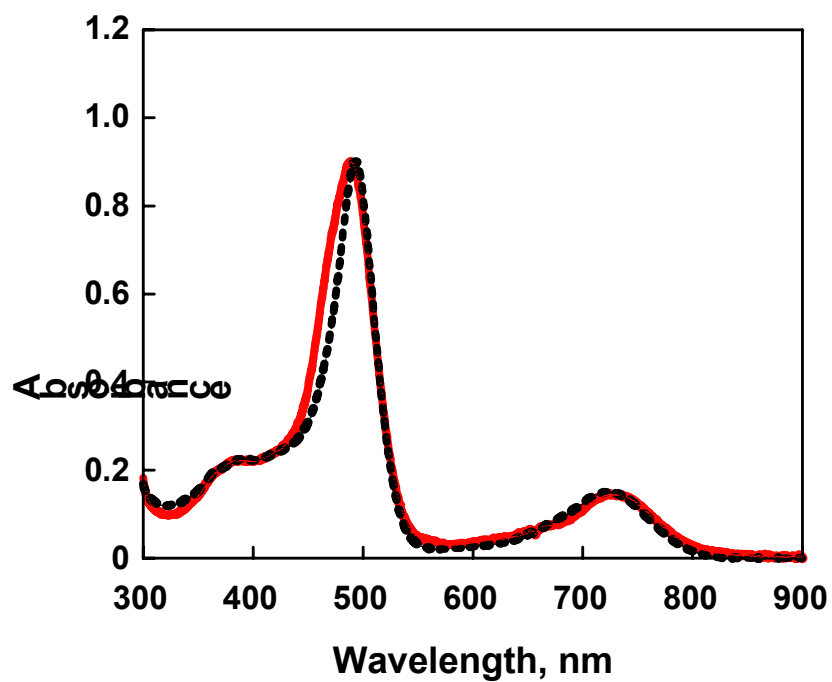


Fig. S5 Absorption spectra of single crystals of **1** (a) and **2** (b) in PhCN (red lines). Dotted lines are spectra obtained upon addition of 1 eq of 2-AN-SO₃H for (a) and 0.5 eq of 2,6-AN-(SO₃H)₂ for (b).

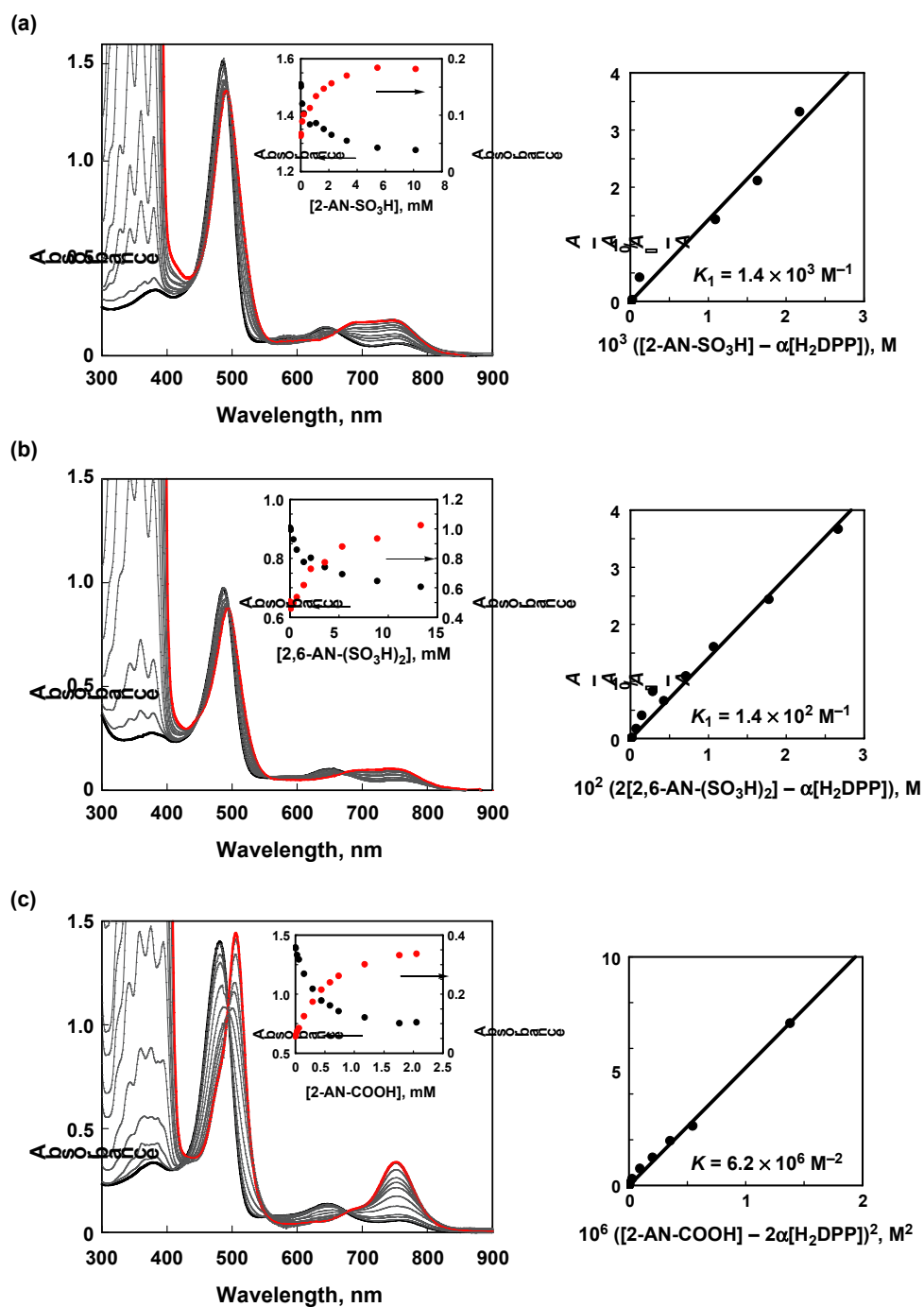


Fig. S6 Absorption spectral change in the course of titration of H₂DPP in DMSO with 2-AN-SO₃H (a), 2,6-AN-(SO₃H)₂ (b), and 2-AN-COOH (c). Inset: (a) Absorbance change at 480 nm (red line) and 505 nm (black line); (b) that at 493 nm (red line) and 470 nm (black line); (c) that at 750 nm (red line) and 480 nm (black line). The concentration of H₂DPP were 1.1×10^{-5} M for 2-AN-SO₃H, 7.0×10^{-6} M for 2,6-AN-(SO₃H)₂ and 1.0×10^{-5} M for 2-AN-COOH.

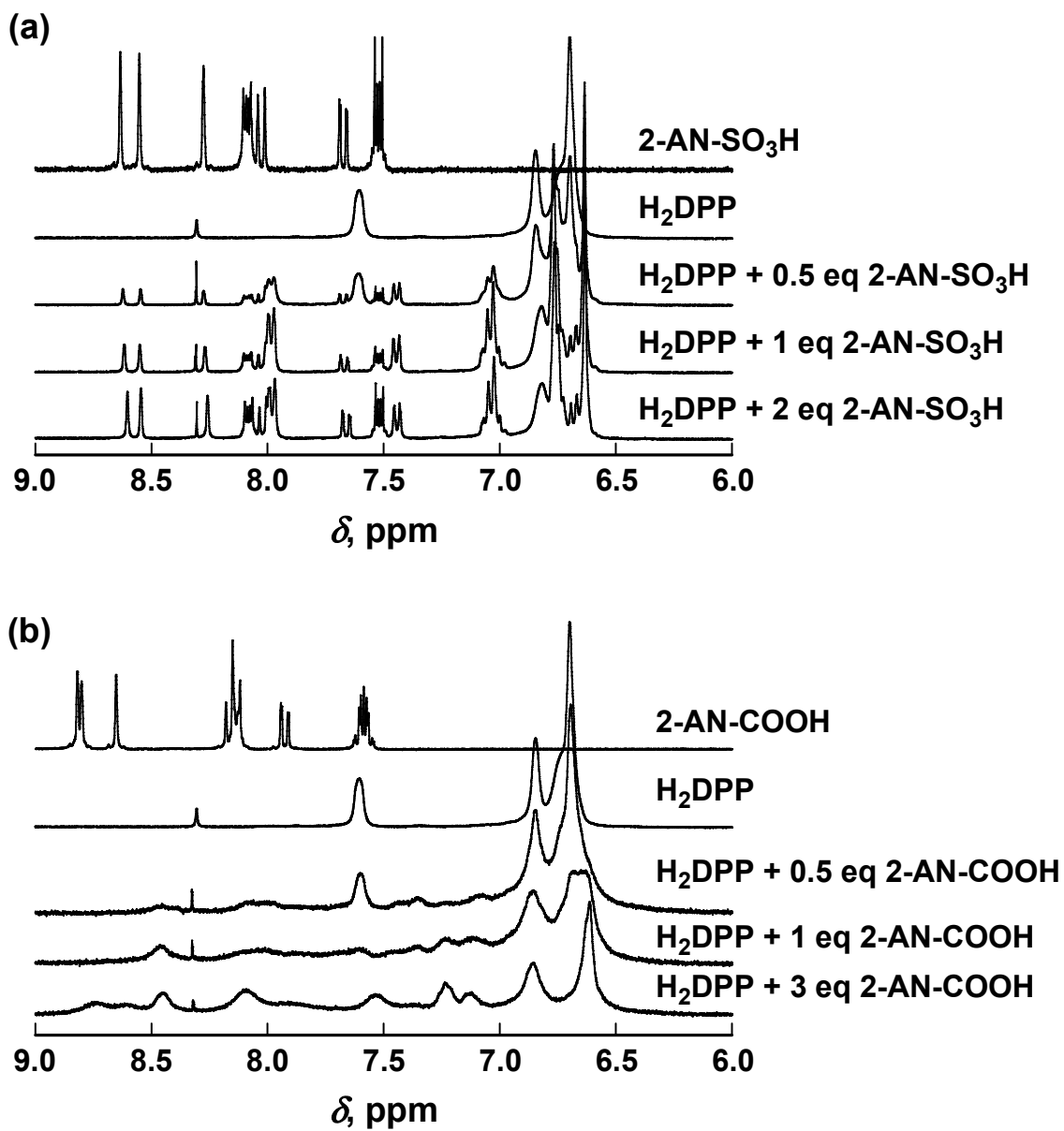


Fig. S7 ¹H NMR spectral change of H₂DPP upon addition of 2-AN-SO₃H (a) and 2-AN-COOH (b) in DMSO-*d*₆ at room temperature.

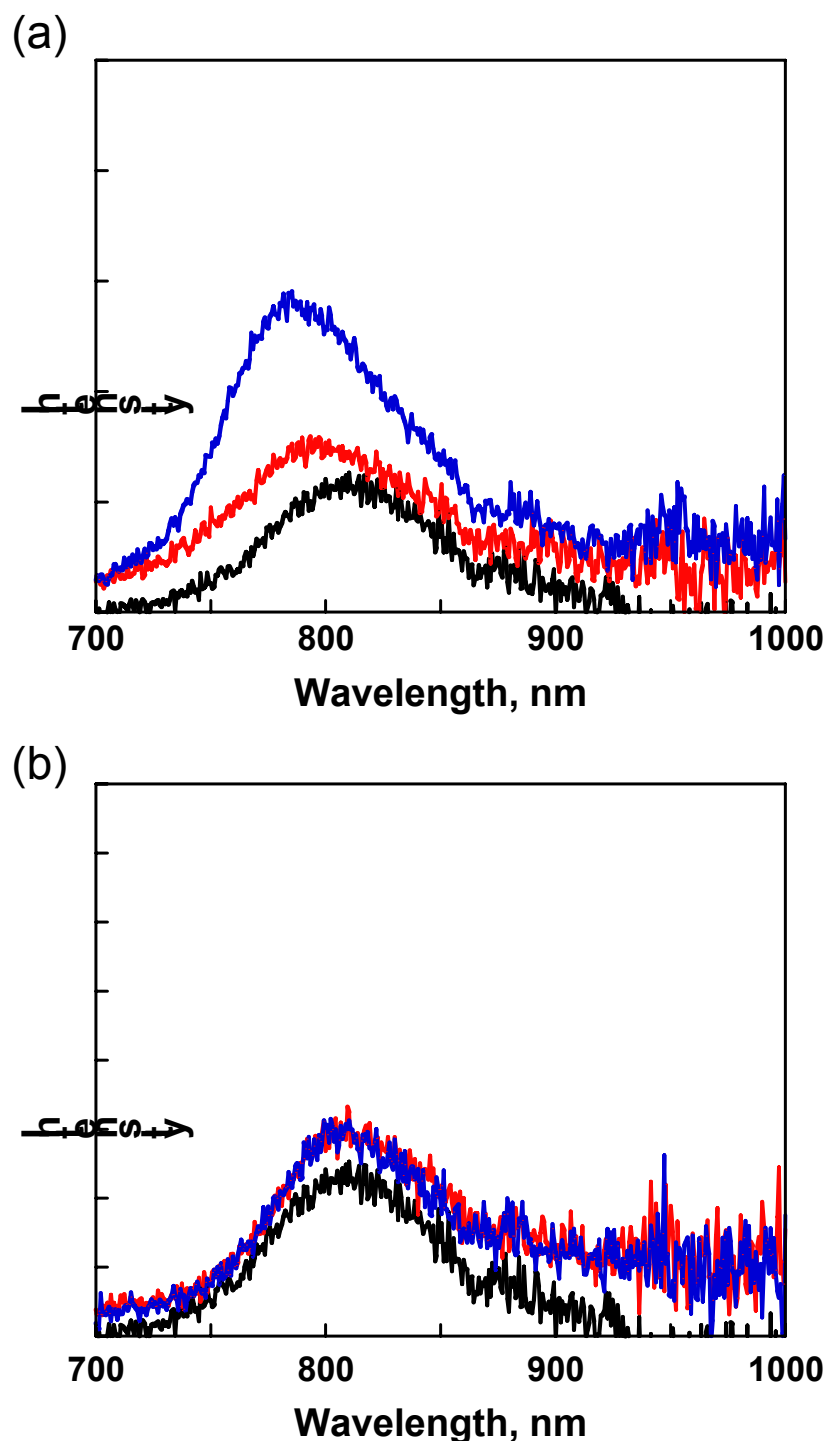


Fig. S8 Change of fluorescence spectra of H₂DPP (black line) in PhCN with photoexcitation at 450 nm upon addition of 2-AN-SO₃H (a) and 2-AN-COOH (b): Red line, addition of 1 eq of the corresponding acid; blue line, addition of 2 eq of the corresponding acid.

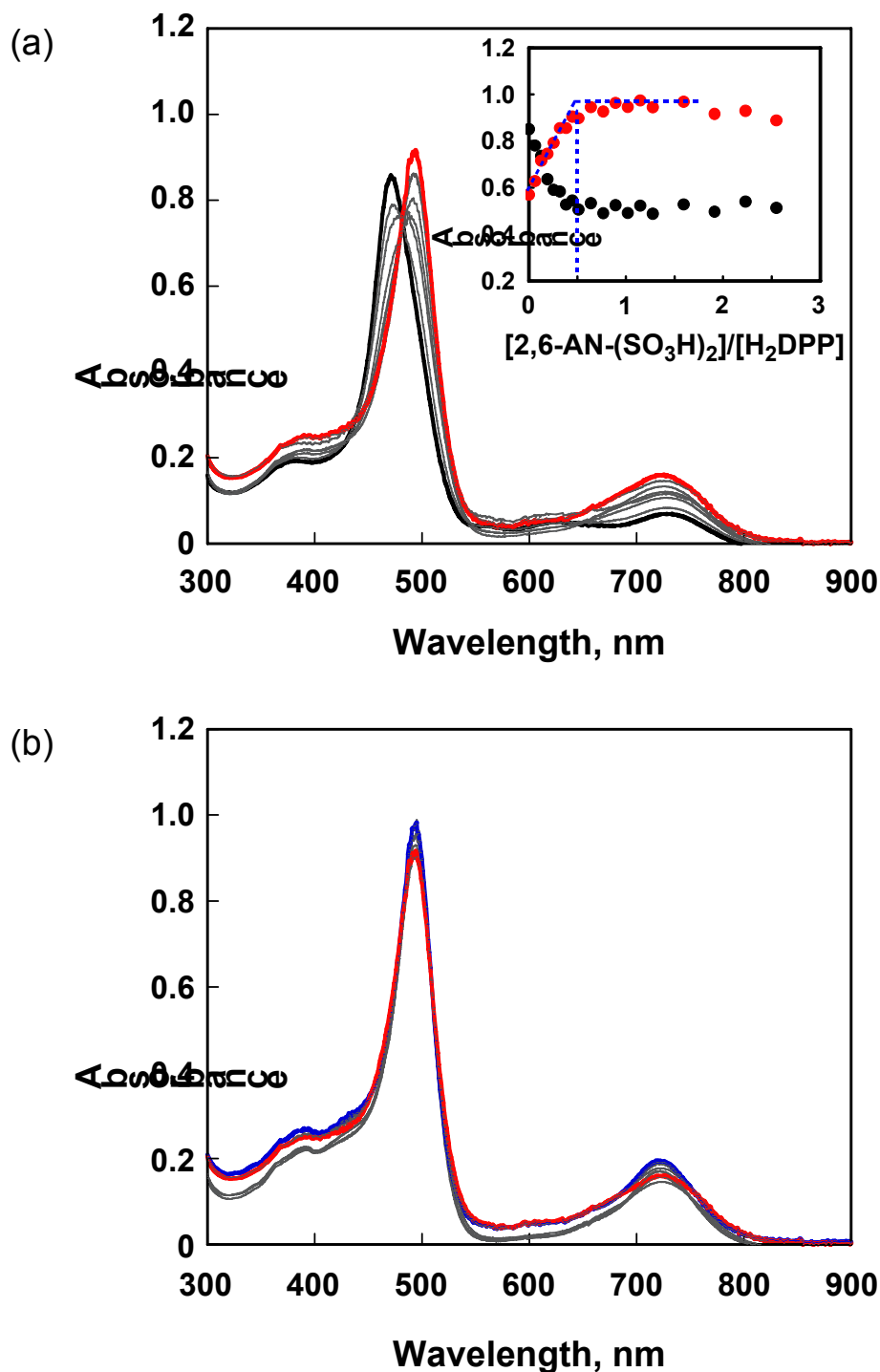


Fig. S9 Absorption spectral change in the course of titration of H₂DPP with 2,6-AN-(SO₃H)₂ in PhCN at room temperature: (a) addition of 0 - 0.5 eq of the acid (inset: absorbance change at 493 nm (red dots) and 470 nm (black dots)); (b) addition of 0.5 - 2.5 eq of the acid. The concentration of H₂DPP was 6.7×10^{-5} M.

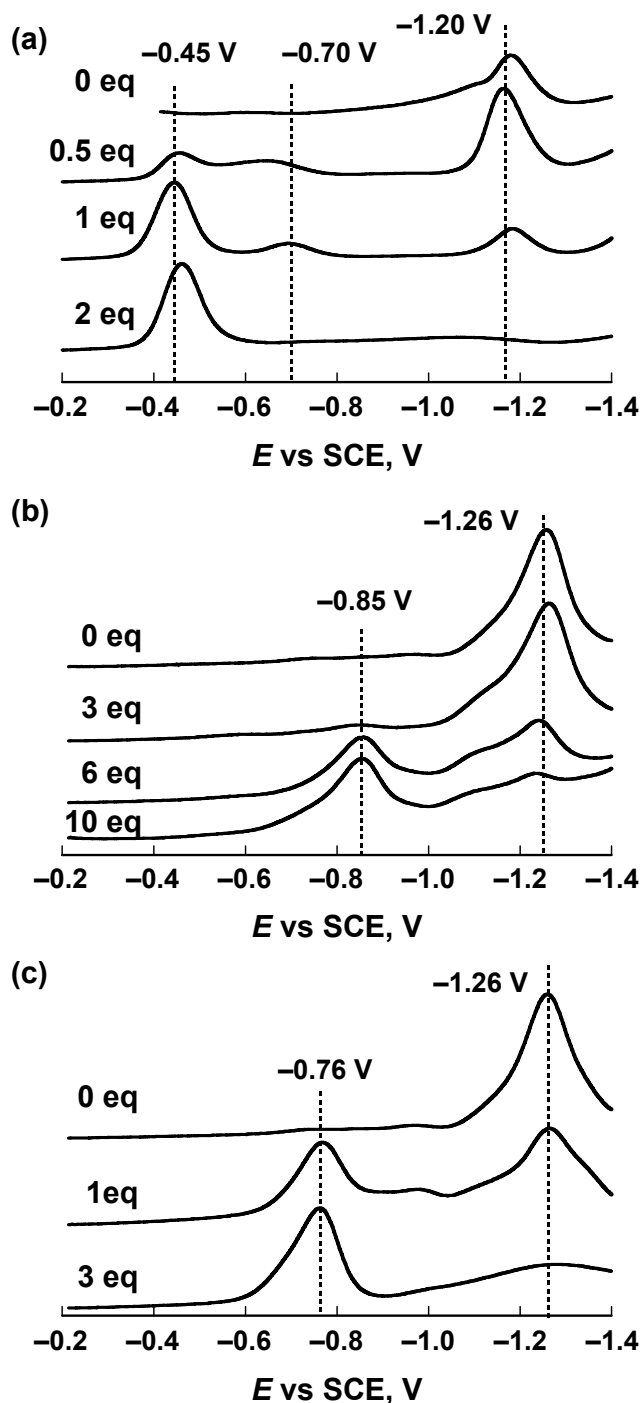


Fig. S10 DPV traces for H₂DPP upon addition of 2-AN-SO₃H in PhCN (a) and 2-AN-SO₃H in DMSO (b) and 2-AN-COOH in DMSO (c): Measured in the presence of 0.1 M [(*n*-butyl)₄N]PF₆ as an electrolyte under Ar at room temperature. The number of equivalents of acid added in each step is given in the figure.

List of Authors of ref 16.

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, J. T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford, CT, 2004.