Supplementary Information

Selective iodinated dipyrrolyldiketone BF_2 complexes as potential building units for oligomeric systems

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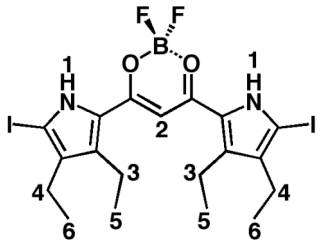
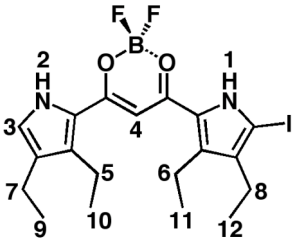
1. Complete ^{1}H NMR assignments of BF_2 complexes

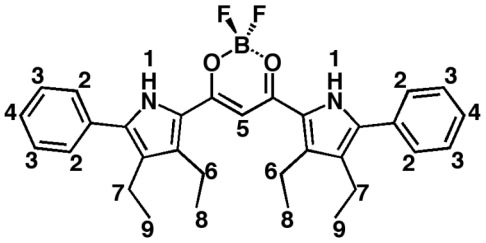
2a-I$_2$: ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.45 (s, 2H, **H-1**), 6.35 (s, 1H, **H-2**), 2.78 (q, J = 7.8 Hz, 4H, **H-3**), 2.42 (q, J = 7.8 Hz, 4H, **H-4**), 1.25 (t, J = 7.8 Hz, 6H, **H-5**), 1.10 (t, J = 7.8 Hz, 6H, **H-6**).



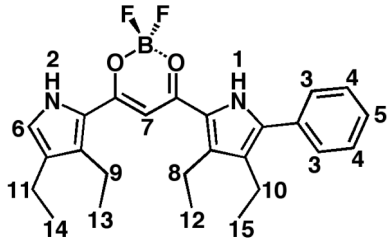
2a-I$_1$: ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.42 (s, 1H, **H-1**), 9.34 (s, 1H, **H-2**), 6.92 (d, J = 3.0 Hz, 1H, **H-3**), 6.42 (s, 1H, **H-4**), 2.78 (qq, J = 7.8 Hz, 4H, **H-5,6**), 2.48 (q, J = 7.8 Hz, 2H, **H-7**), 2.43 (q, J = 7.8 Hz, 2H, **H-8**), 1.25 (tt, J = 7.8 Hz, 6H, **H-9**), 1.21 (t, J = 7.8 Hz, 3H, **H-10,11**), 1.10 (t, J = 7.8 Hz, 3H, **H-12**).



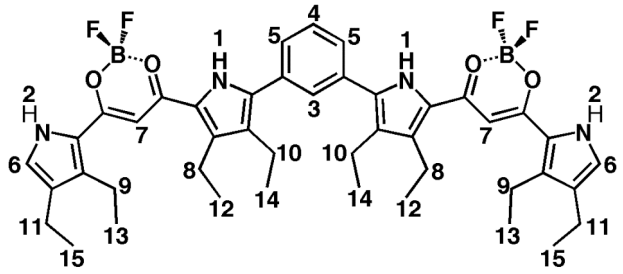
2b: ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.37 (s, 1H, **H-1**), 7.53–7.51 (m, 4H, **H-2**), 7.50–7.48 (m, 4H, **H-3**), 7.43–7.39 (m, 2H, **H-4**), 6.56 (s, 1H, **H-5**), 2.86 (q, J = 7.8 Hz, 4H, **H-6**), 2.62 (q, J = 7.8 Hz, 4H, **H-7**), 1.35 (t, J = 7.8 Hz, 6H, **H-8**), 1.20 (t, J = 7.8 Hz, 6H, **H-9**).



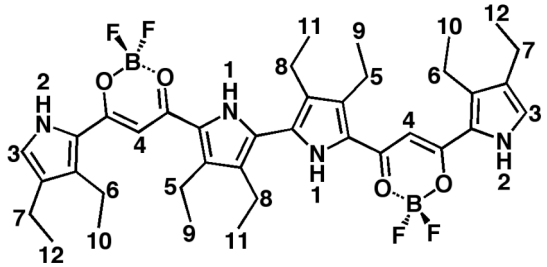
2c: ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.32 (s, 1H, **H-1**), 9.29 (s, 1H, **H-2**), 7.55–7.51 (m, 2H, **H-3**), 7.50–7.47 (m, 2H, **H-4**), 7.43–7.40 (m, 1H, **H-5**), 6.94 (d, J = 3.0 Hz, 1H, **H-6**), 6.52 (s, 1H, **H-7**), 2.85 (q, J = 7.8 Hz, 2H, **H-8**), 2.80 (q, J = 7.8 Hz, 2H, **H-9**), 2.61 (q, J = 7.8 Hz, 2H, **H-10**), 2.49 (q, J = 7.8 Hz, 2H, **H-11**), 1.33 (t, J = 7.8 Hz, 3H, **H-12**) 1.28 (t, J = 7.8 Hz, 3H, **H-13**), 1.22 (t, J = 7.8 Hz, 3H, **H-14**), 1.19 (t, J = 7.8 Hz, 3H, **H-15**).



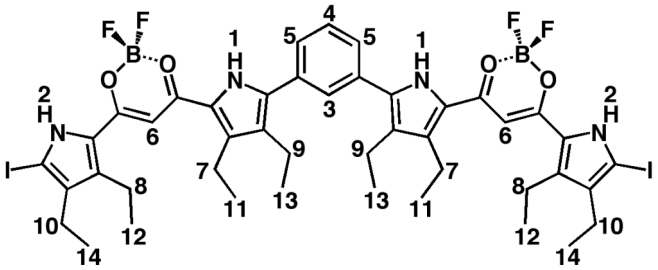
3a: ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.39 (s, 2H, **H-1**), 9.30 (s, 2H, **H-2**), 7.64 (s, 1H, **H-3**), 7.59–7.58 (m, 1H, **H-4**), 7.53 (m, 2H, **H-5**), 6.94 (s, 2H, **H-6**), 6.53 (s, 2H, **H-7**), 2.84–2.82 (m, 4H, **H-8**), 2.82–2.80 (m, 4H, **H-9**), 2.64 (m, 4H, **H-10**), 2.48 (m, 4H, **H-11**), 1.30 (m, 6H, **H-12**), 1.27 (m, 6H, **H-13**), 1.20 (m, 12H, **H-14,15**).



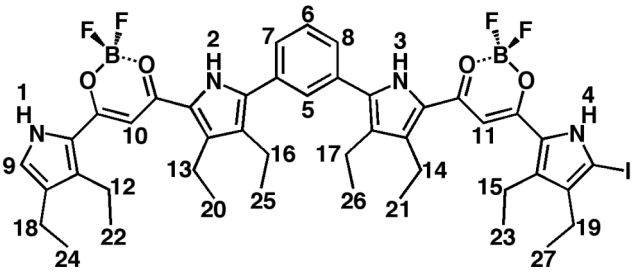
3b: ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.32 (s, 1H, **H-1**), 9.27 (s, 1H, **H-2**), 6.98 (d, J = 3.0 Hz, 2H, **H-3**), 6.54 (s, 1H, **H-4**), 2.87–2.84 (m, 4H, **H-5**), 2.83–2.79 (m, 4H, **H-6**), 2.61 (q, J = 7.8 Hz, 4H, **H-7**), 2.49 (q, J = 7.8 Hz, 4H, **H-8**), 1.34 (t, J = 7.8 Hz, 6H, **H-9**), 1.28 (t, J = 7.8 Hz, 6H, **H-10**), 1.22 (t, J = 7.8 Hz, 6H, **H-11**), 1.16 (t, J = 7.8 Hz, 6H, **H-12**).



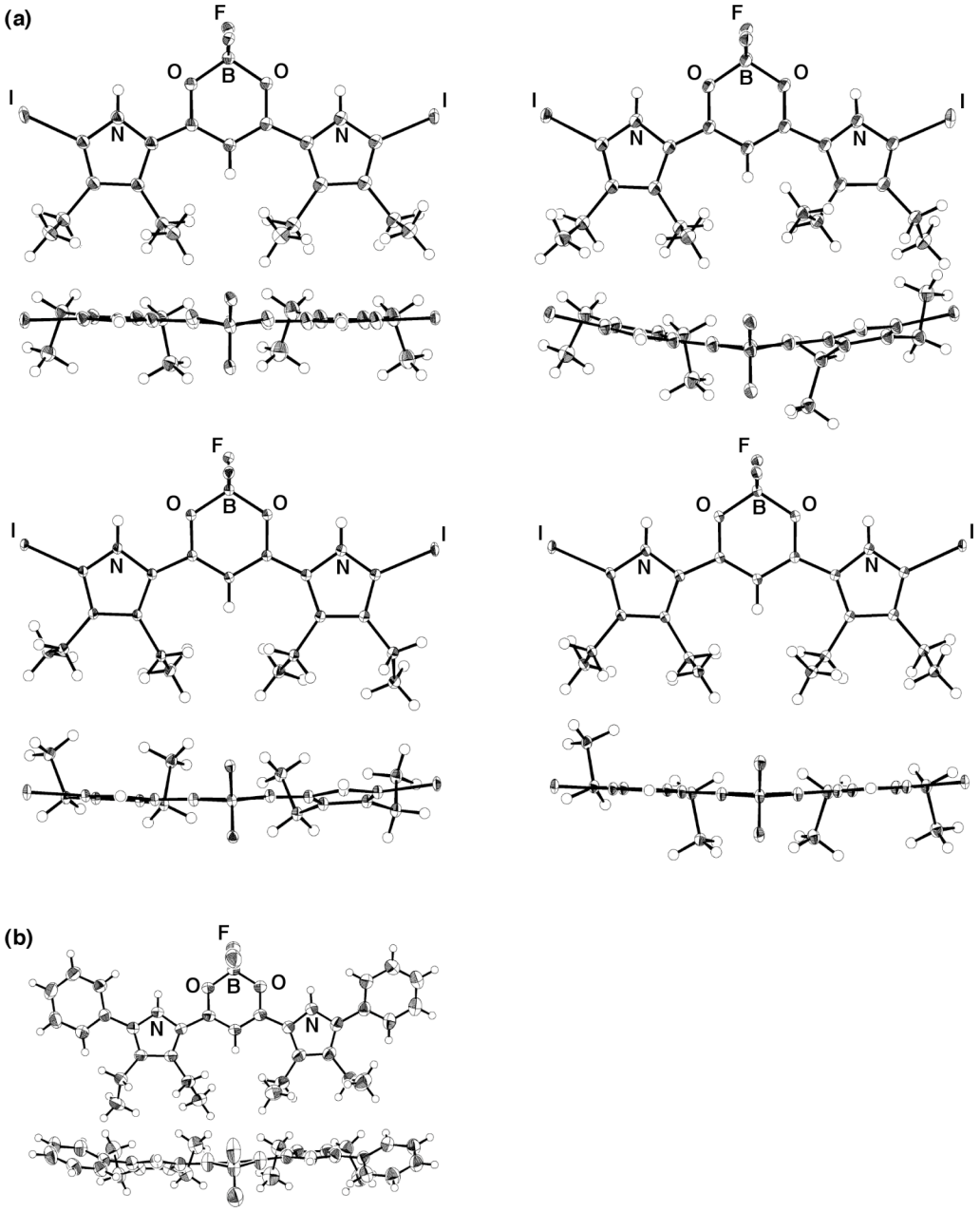
3a-I$_2$: ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.42 (s, 2H, **H-1**), 9.41 (s, 2H, **H-2**), 7.64 (s, 1H, **H-3**), 7.63–7.60 (m, 1H, **H-4**), 7.56–7.54 (m, 2H, **H-5**), 6.48 (s, 2H, **H-6**), 2.84 (q, J = 7.8, 8H, **H-7,8**), 2.65 (q, J = 7.8 Hz, 4H, **H-9**), 2.43 (q, J = 7.8 Hz, 4H, **H-10**), 1.34 (t, J = 7.8 Hz, 6H, **H-11**), 1.29 (t, J = 7.8 Hz, 6H, **H-12**), 1.20 (t, J = 7.8 Hz, 6H, **H-13**), 1.11 (t, J = 7.8 Hz, 6H, **H-14**).



3a-I$_1$: ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.39 (s, 3H, **H-1–3**), 9.29 (s, 1H, **H-4**), 7.64 (s, 1H, **H-5**), 7.60 (m, 1H, **H-6**), 7.51–7.42 (m, 2H, **H-7,8**), 6.93 (s, 1H, **H-9**), 6.51 (s, 1H, **H-10**), 6.45 (s, 1H, **H-11**), 2.82–2.78 (m, 8H, **H-12–15**), 2.64–2.63 (m, 4H **H-16,17**), 2.46 (m, 2H, **H-18**), 2.42–2.41 (m, 2H, **H-19**), 1.32 (m, 6H, **H-20,21**), 1.26 (m, 6H, **H-22,23**), 1.20–1.17 (m, 9H, **H-24–26**), 1.09 (t, J = 7.8 Hz, 3H, **H-27**).

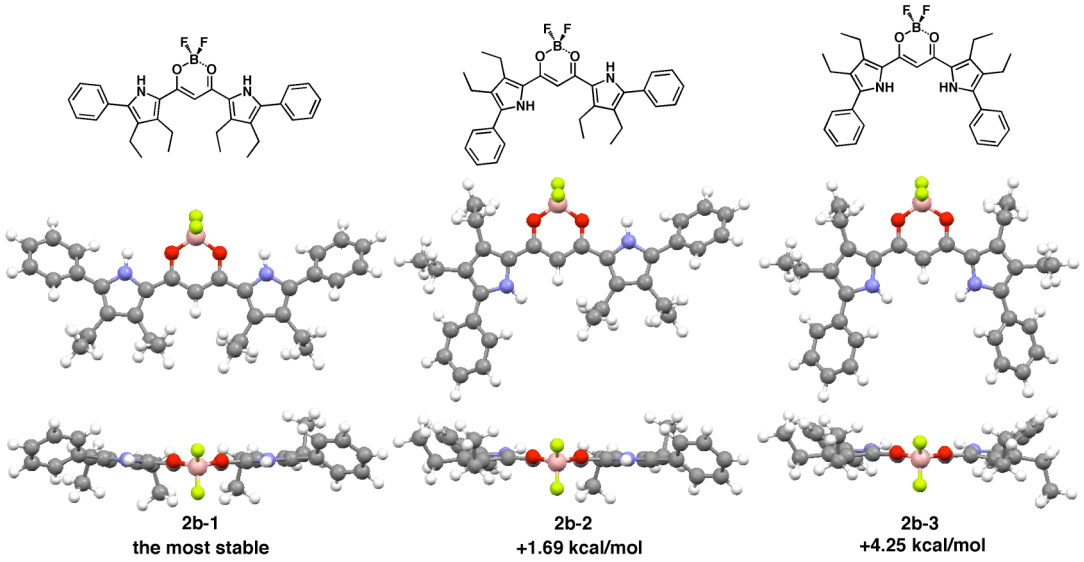


2. X-ray crystallographic data for 2a-I_2 and 2b

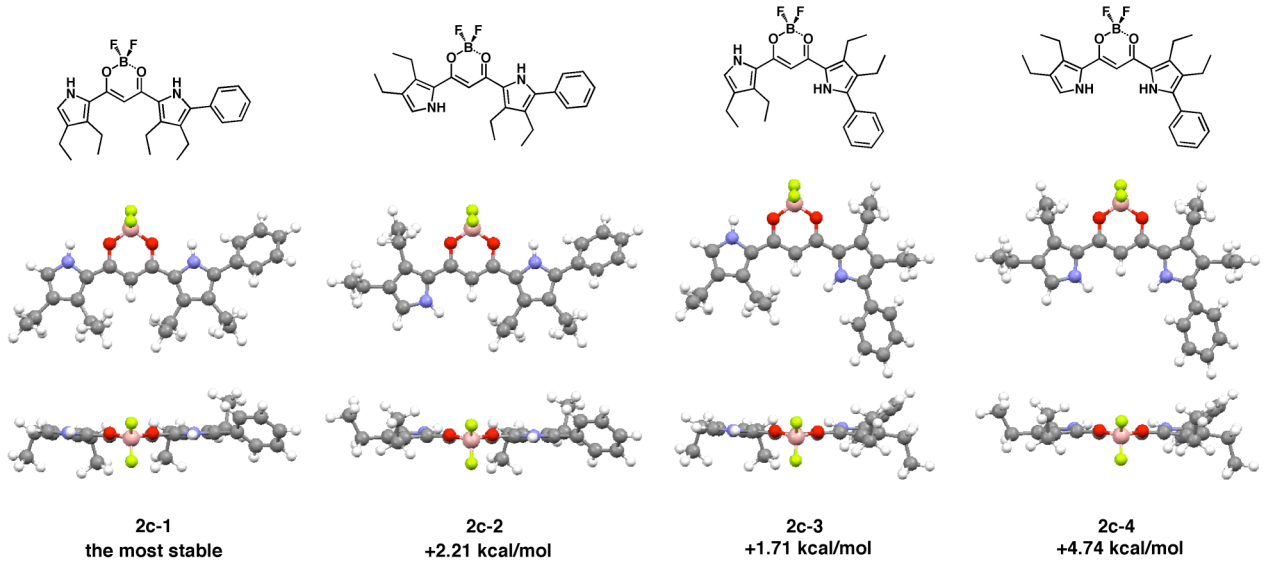


Supporting Figure 1 Ortep drawings (top and side view) of X-ray single crystal structures of (a) **2a-I_2** (four independent conformations) and (b) **2b**. Thermal ellipsoids are scaled to the 50% probability level.

3. Optimization of dipyrrolyldiketone BF_2 complexes by DFT calculations[S3]



Supporting Figure 2 Optimized structures of **2b** (three conformations) at B3LYP/6-31G(d,p).



Supporting Figure 3 Optimized structures of **2c** (four conformations) at B3LYP/6-31G(d,p).

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Cartesian Coordination of 2b-3.

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Cartesian Coordination of 2c-1.

–1454.8937159 hartree

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Cartesian Coordination of 2c-2.

–1454.8902002 hartree

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H,0.1801573727,2.7327547516,-1.9295478561
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C,-4.9789437424,2.1457843984,0.0327541304
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C,-2.2821469971,-0.2500690086,-0.1091514187
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F,-1.0984622132,-3.4576567337,0.5724975764
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Cartesian Coordination of 2c-3.

–1454.8909956 hartree

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H,-3.6445389982,-1.7772187923,-2.6519336598
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Cartesian Coordination of 2c-4.

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C,-2.8759208154,-0.3715836621,-4.6722056181
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F,2.8641714676,0.0557389026,-2.497957751
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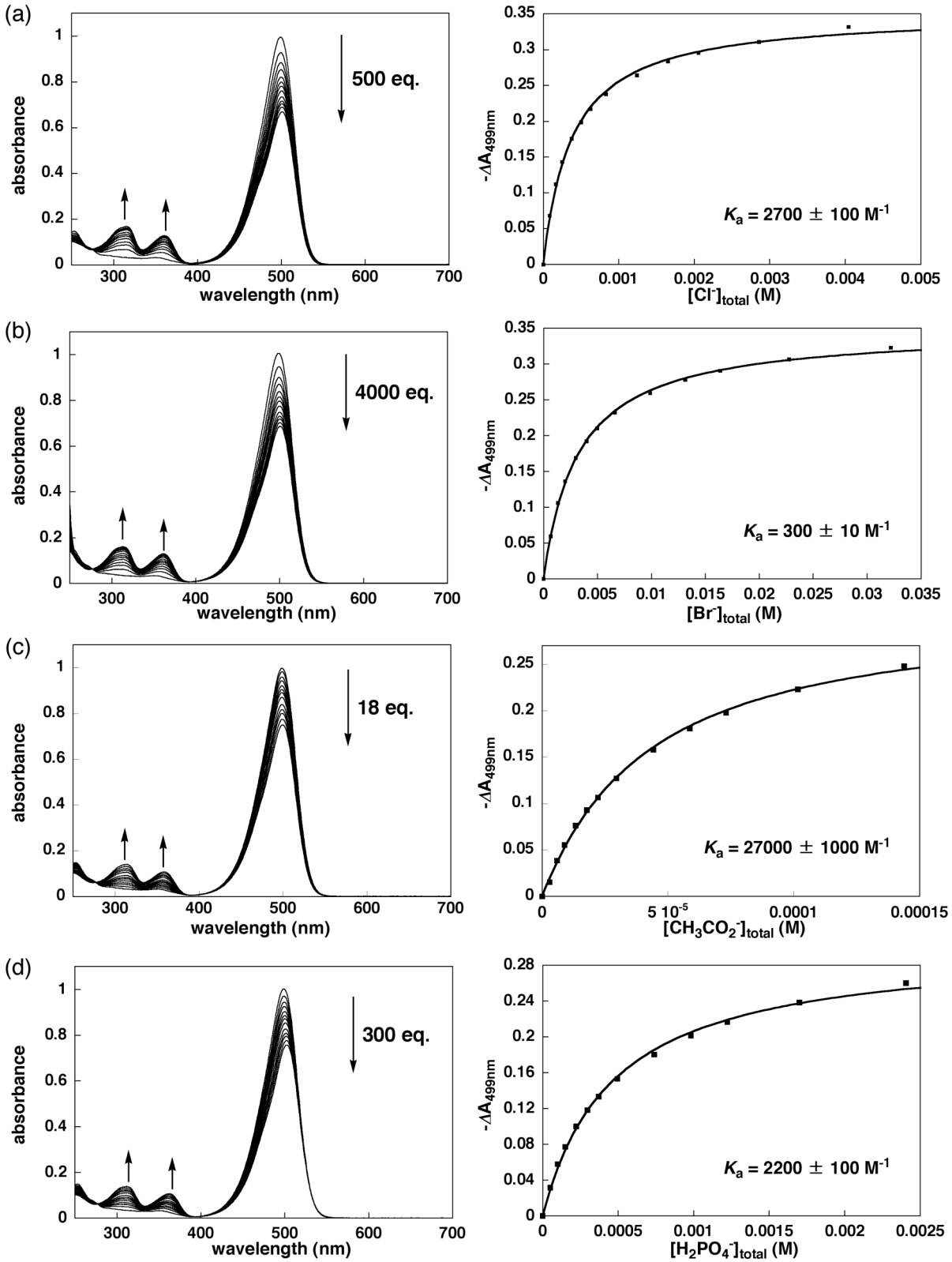
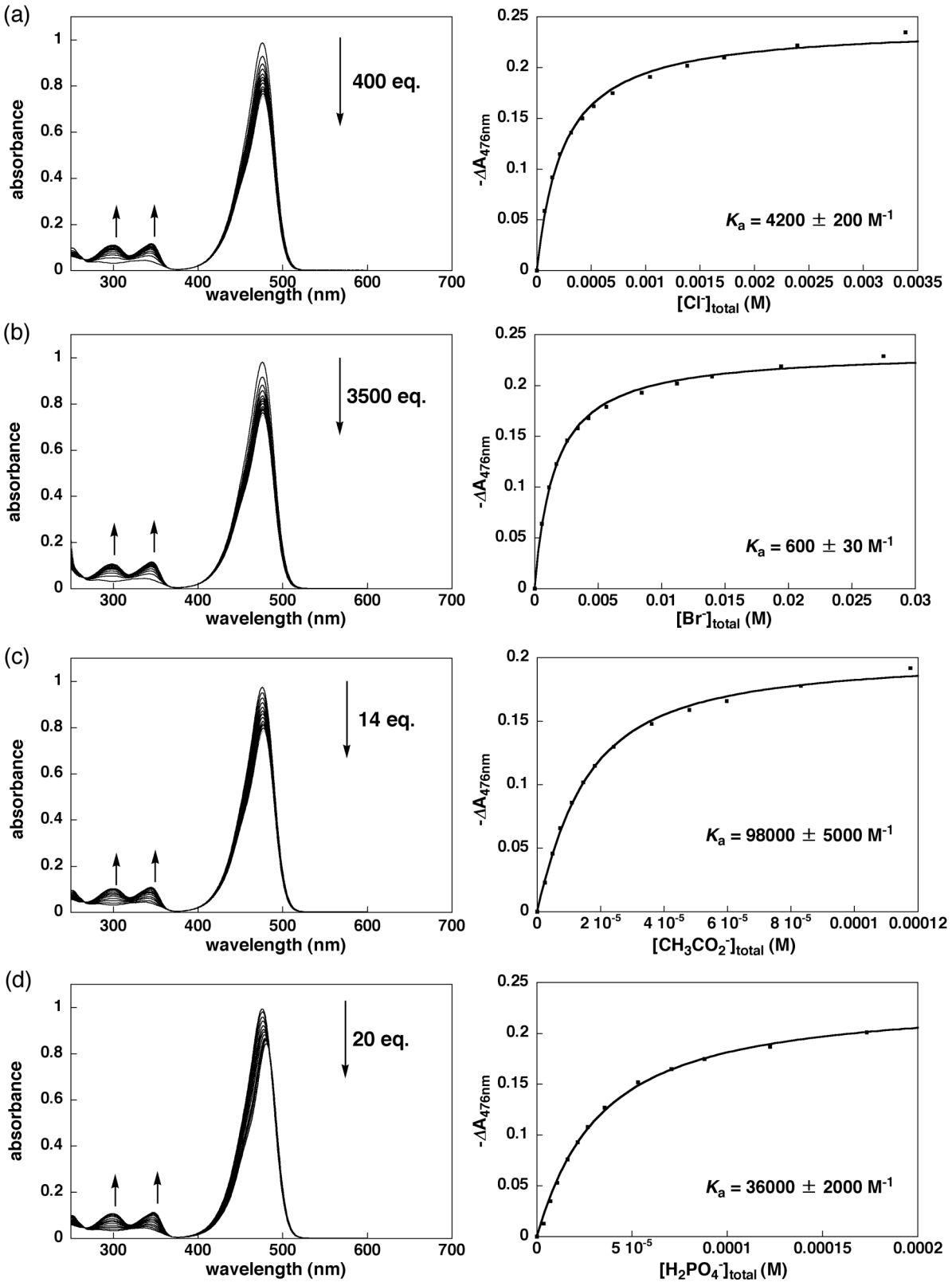
C,-2.8653280729,2.0488538728,6.089379274
C,-1.8799699895,1.1470687964,6.496512411
B,2.1970288464,-1.026477851,-1.9794452087

[S3] *Gaussian 03*, (Revision C.01), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., 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, V. Bakken, 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, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

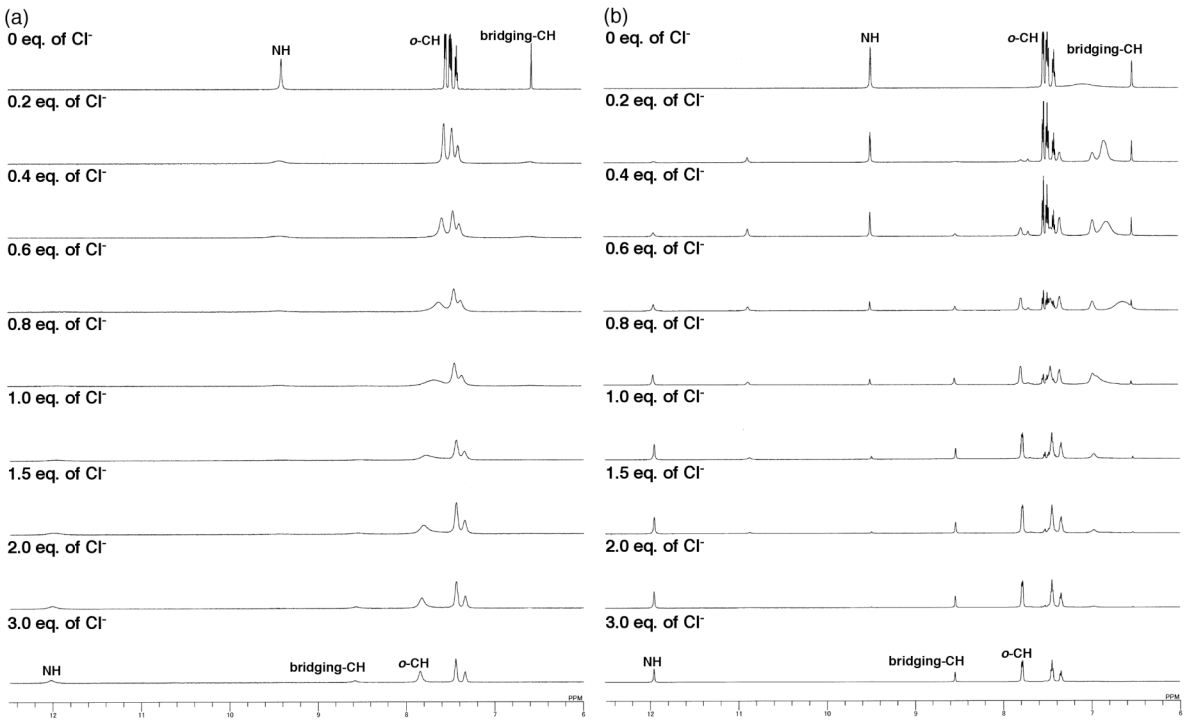
4. Anion binding behavior



Supporting Figure 4 UV/vis absorption spectral changes (left) and corresponding titration plots and 1:1 fitting curves (right) of **2b** (8.2×10^{-6} M) upon the addition of (a) Cl^-, (b) Br^-, (c) $CH_3CO_2^-$, and (d) $H_2PO_4^-$ as tetrabutylammonium salts in CH_2Cl_2.



Supporting Figure 5 UV/vis absorption spectral changes (left) and corresponding titration plots and 1:1 fitting curves (right) of **2c** (8.8×10^{-6} M) upon the addition of (a) Cl^-, (b) Br^-, (c) $CH_3CO_2^-$ and (d) $H_2PO_4^-$ as tetrabutylammonium salts in CH_2Cl_2.



Supporting Figure 6 ^{1}H NMR spectral changes of **2b** (1.0×10^{-3} M) in CD_2Cl_2 at (a) r.t. and (b) –50 °C upon the addition of Cl^- (0–3.0 equiv) added as a tetrabutylammonium salt.