Electronic Supplementary Information

Optical Property Control of π-Electronic Systems Bearing Lewis Pairs by Ion Coordination

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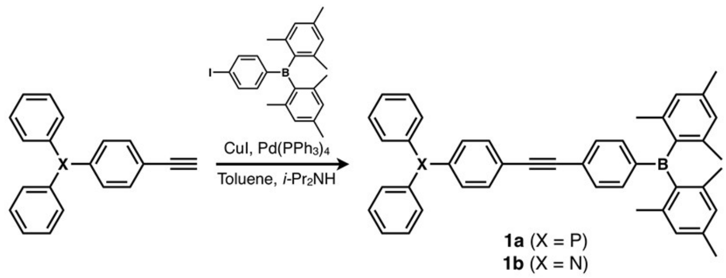
1. Synthetic procedures and spectroscopic data

General procedures. Starting materials were purchased from Kanto Chemical, TCI, and Sigma-Aldrich, and used without further purification unless otherwise stated. All reactions were performed under dry nitrogen atmosphere unless otherwise noted. ^{1}H, ^{13}C, ^{11}B, and ^{31}P NMR spectra used in the characterization of products were recorded on a JEOL ECZ-600 (^{1}H: 600 MHz, ^{13}C: 150 MHz, ^{11}B: 115 MHz, ^{31}P: 242 MHz) spectrometer with chemical shifts (in ppm) relative to tetramethylsilane (^{1}H), solvent (^{13}C), BF_3 (^{11}B), and H_3PO_4 (^{31}P) as references. UV-visible absorption spectra were recorded on JASCO V-750ST spectrometer using a 10 mm quartz cell. Fluorescence spectra were recorded on JASCO FP-8600 fluorescence spectrometer. Quantum yield (QY) measurements have been carried out by using Hamamatsu absolute quantum yield measurement system C9920-02G TLC analyses were carried out on aluminum sheets coated with silica gel 60 (Merck 5554). Column chromatography was performed on Mightysil Si60 (Kanto Chemical).



Synthesis of 1a

4-Diphenylphosphinophenylacetylene[S1] (0.22 g, 0.77 mmol), CuI (4.7 mg, 0.025 mmol), and $Pd(PPh_3)_4$ (28 mg, 0.025 mmol) were added to a solution of (4-iodophenyl)dimesitylborane[S2] (0.23 g, 0.51 mmol) in toluene (20 mL) and *i*-Pr_2NH (10 mL), and the mixture was stirred overnight at 80 °C. After CH_2Cl_2 was added, the reaction mixture was washed with saturated aq. NH_4Cl. A combined organic phase was dried over Na_2SO_4 and solvents were removed by a rotary evaporator. The residue was chromatographed over silica gel column (SiO_2; eluent: hexane/ethyl acetate = 1/3) to afford **1a** as a white solid (0.37 g, quant). R_f = 0.4 (chloroform/hexane = 5/1); ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.49 (4H, s), 7.37–7.30 (14H), 6.82 (4H, s), 2.31 (6H, s), 2.00 (12H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ (ppm) 140.82, 138.84, 136.62, 136.55, 136.08, 133.88, 133.75, 133.47, 133.34, 131.50, 131.06, 128.94, 128.60, 128.21, 126.33, 123.24, 91.16, 90.70, 23.41, 21.22; ^{11}B-NMR (192 MHz, CH_2Cl_2) δ (ppm) 73.24; ^{31}P-NMR (242 MHz, CH_2Cl_2) δ (ppm) –4.45. HRESI-TOF-MS: *m/z* (% intensity): 611.3045 (100). Calcd for $C_{44}H_{41}BP$ ($[M+H]^+$): 611.3041.

Synthesis of 1b

4-Diphenylaminophenylacetylene[S3] (0.26 g, 0.96 mmol), CuI (6.1 mg, 0.032 mmol), and $Pd(PPh_3)_4$ (0.037 g, 0.032 mmol) were added to a solution of (4-iodophenyl)dimesitylborane[S2] (0.29 g, 0.64 mmol) in toluene (27 mL) and *i*-Pr_2NH (13 mL) at 80 °C, and the mixture was stirred overnight. After CH_2Cl_2 was added, the reaction mixture was washed with saturated aq. NH_4Cl. A combined organic phase was dried over Na_2SO_4 and solvents were removed by a rotary evaporator. The residue was chromatographed over silica gel column (SiO_2; eluent: hexane/$CHCl_3$ = 3/2) to afford **1b** as a yellow solid (0.31 g, 0.52 mmol, 81%). R_f = 0.6 (hexane/$CHCl_3$ = 3/2); ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.47 (4H, m), 7.37 (2H, d, J = 8.1 Hz), 7.28 (4H, dd, J = 7.6, 7.2 Hz), 7.11 (4H, d, J = 7.2 Hz), 7.07 (2H, t, J = 7.6 Hz), 7.00 (2H, d, J = 8.1 Hz), 6.82 (4H, s), 2.31 (6H, s), 2.00 (12H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ (ppm) 148.10, 147.10, 145.37, 141.54, 140.81, 138.75, 136.14, 132.62, 130.86, 129.39, 128.19, 126.99, 125.05, 123.62, 122.08, 115.69, 91.99, 89.01, 23.42, 21.22; ^{11}B-NMR (192 MHz, CH_2Cl_2) δ (ppm) 72.80. ESI-TOF-MS: *m/z* (% intensity): 593.323. Calcd for $C_{44}H_{40}BN$ ($[M]^+$): 593.621.

[S1] Mei, X.; Jiayun, L.; Jiajian, P.; Ying, B.; Guodong, Z.; Wenjun, X.; Guoqiao, L.; *Appl. Organometal. Chem.* 2014, **28**, 120–126.
[S2] Lei, J.; Qi, F.; Mao-sen, Y.; Zhi-qiang, L.; Yu-xiang, S.; Hong-feng, C. *Org. Lett.* 2010, **12**, 5192–5195.
[S3] Krishna, P.; Ravi, M. A.; Thomas, H. K. *J. Phys. Chem. A* 2010, **114**, 4542–4549.

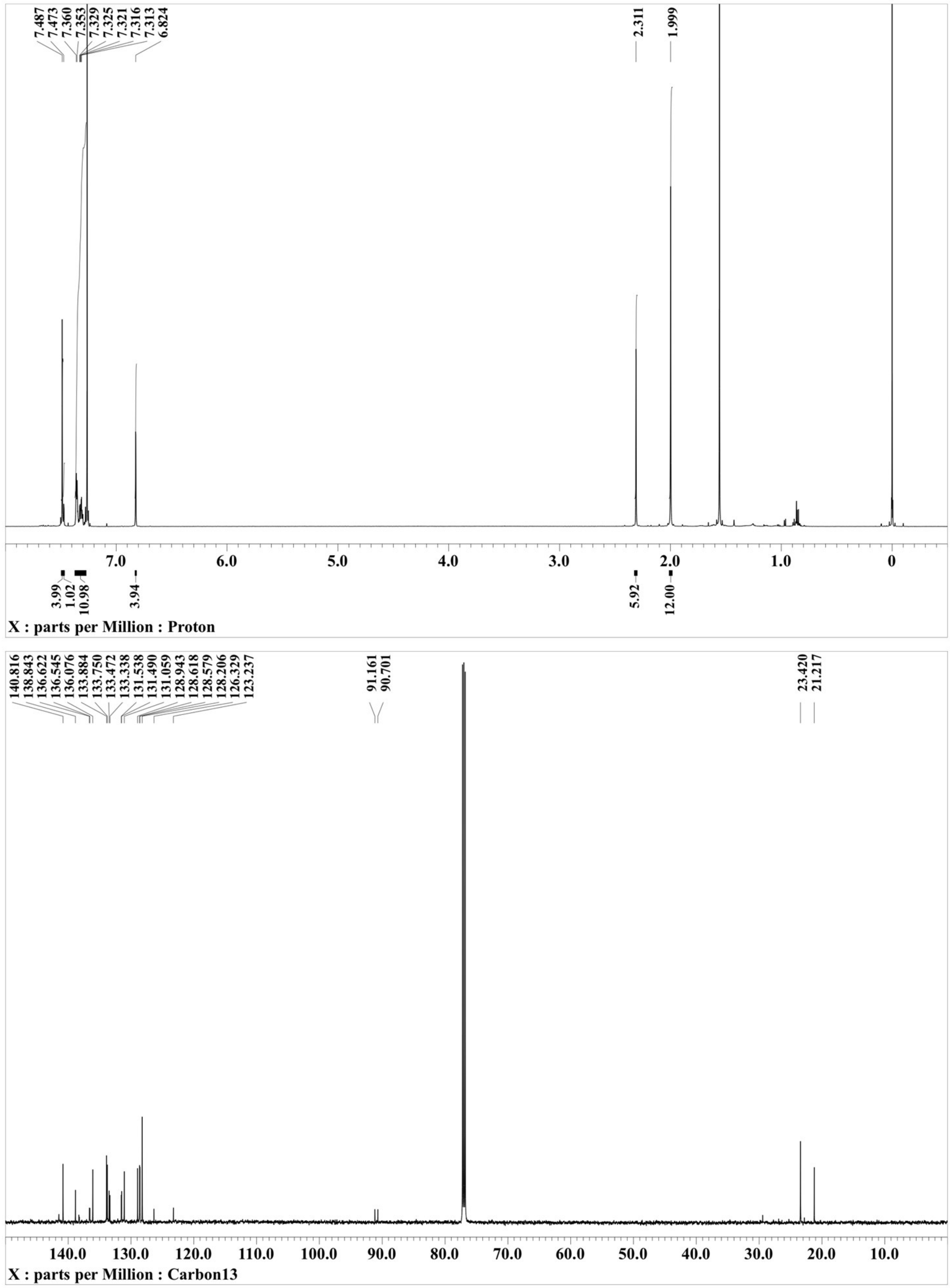
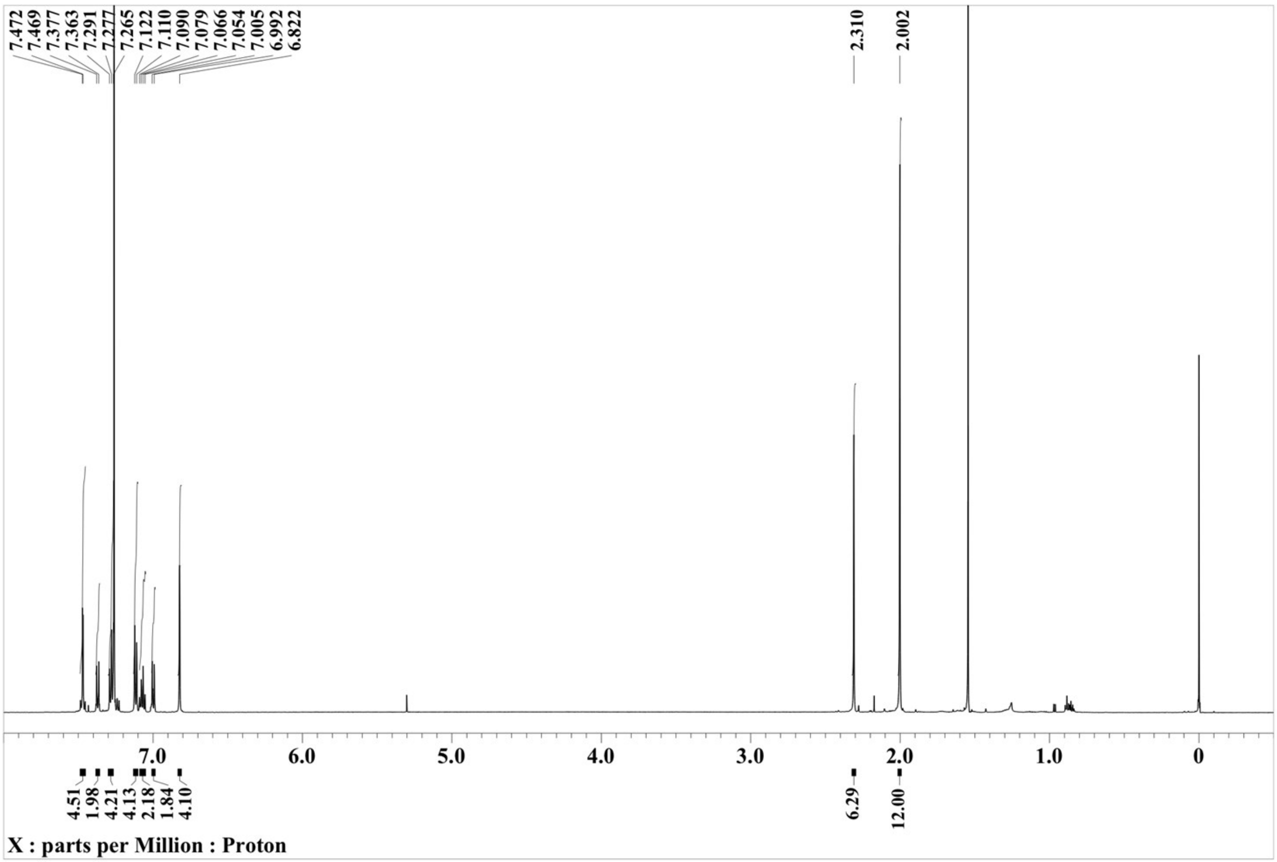


Fig. S1 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **1a** in $CDCl_3$ at 25 °C.



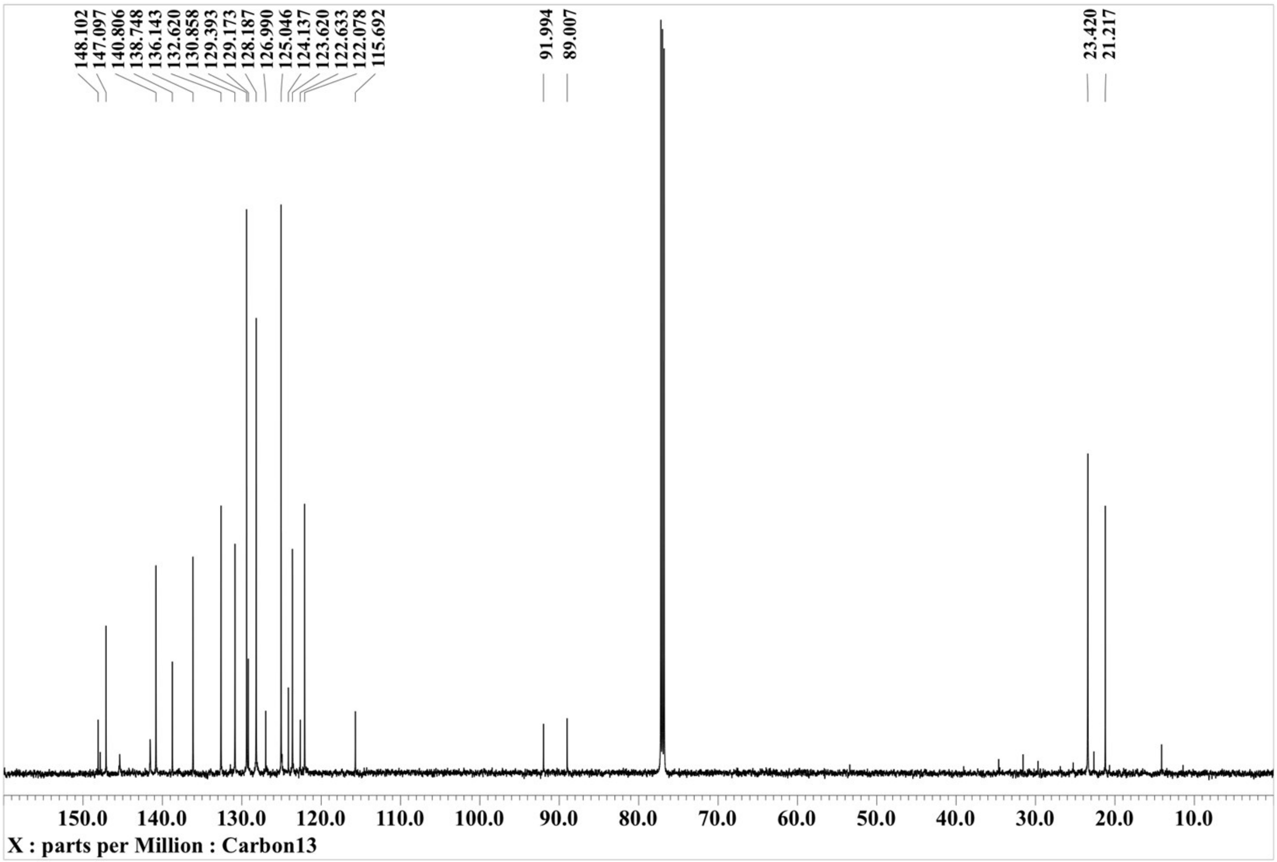


Fig. S2 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **1b** in $CDCl_3$ at 25 °C.

2. Optical properties

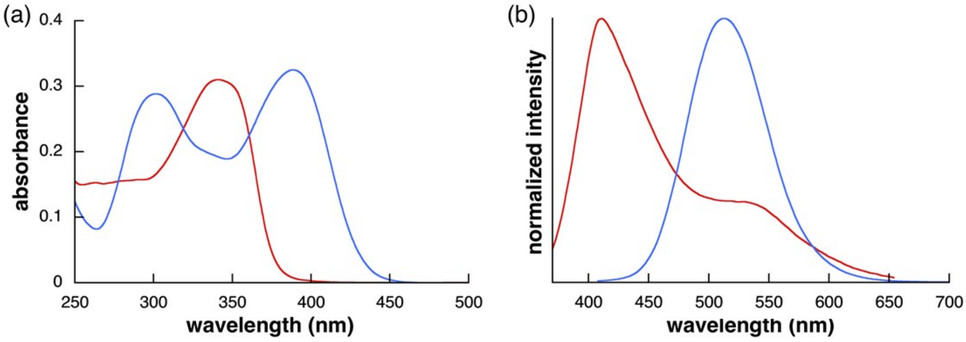


Fig. S3 (a) UV/vis absorption and (b) fluorescence spectra of **1a** (red) and **1b** (blue) in CH_2Cl_2 (10^{-5} M). The fluorescence spectra were obtained by excitation at the respective absorption maxima.

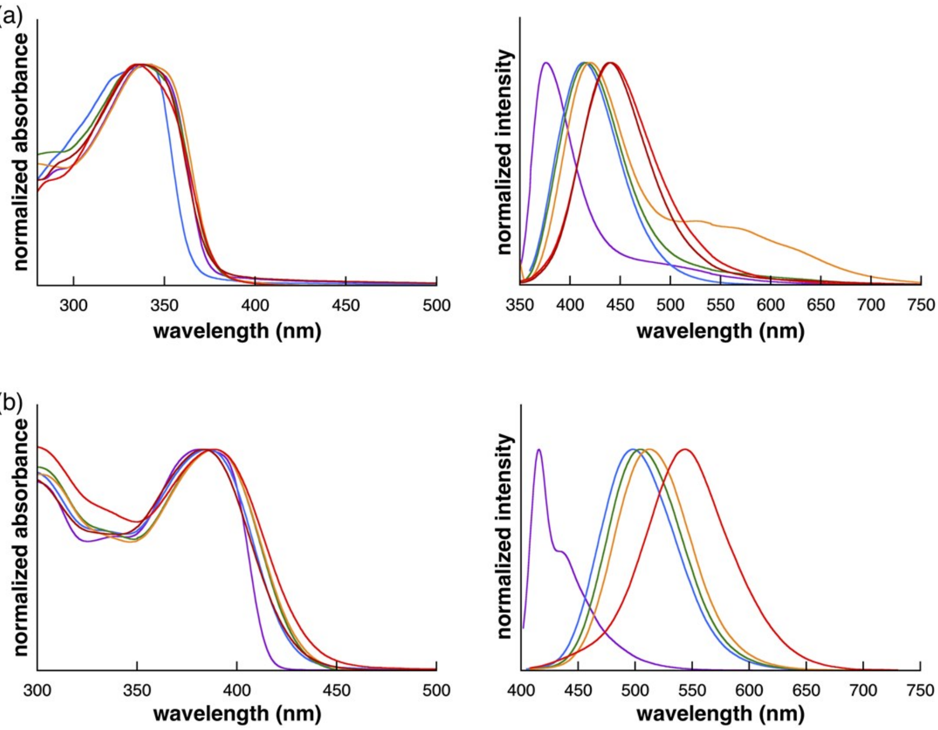


Fig. S4 UV/vis absorption (left) and fluorescence (right) spectra of (a) **1a** and (b) **1b** in hexane (purple), ethyl acetate (blue), THF (green), CH_2Cl_2 (orange), DMF (red), and MeCN (dark red) (10^{-5} M). The fluorescence spectra were obtained by excitation at the respective absorption maxima.

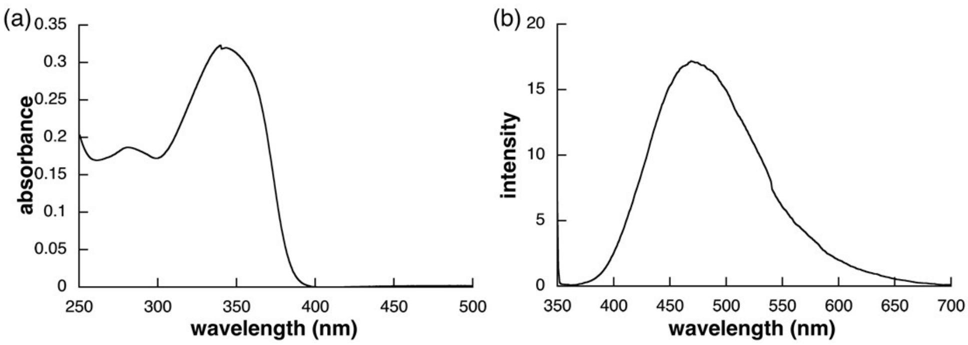


Fig. S5 (a) UV/vis absorption and (b) fluorescence spectra of **1a** in spin-coated film.

Table S1 Fluorescence quantum yields of **1a** and **1b** in CH_2Cl_2, film state, and powder state.

compound	$\Phi_{solution}$ (%)	Φ_{film} (%)	Φ_{powder} (%)
1a	6	27	36
1b	86	49	41

3. Theoretical studies

DFT calculations. DFT calculations of the geometrical optimization were carried out by Gaussian 16 program.[S4] In addition, the solvent (CH_2Cl_2) effect was included through the SCRF-PCM method.[S5] Unless stated, all the structures are confirmed to be minimum-energy structures with no imaginary frequencies. The B3LYP functional was chosen because it well reproduces the energy of the ground state and the lowest singlet (S_1) excited state in all compounds. The lowest six singlet–singlet transitions were computed by the time-dependent density functional theory (TD-DFT) calculation.

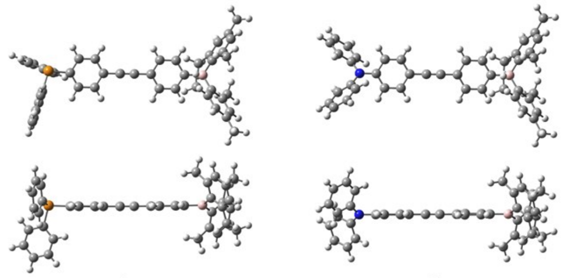


Fig. S6 Optimized structures of **1a** and **1b** at B3LYP/6-31G(d,p) level.

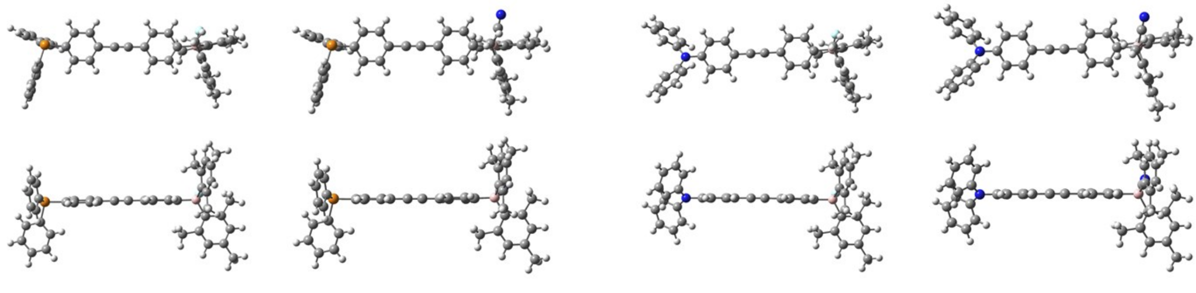


Fig. S7 Optimized structures of **1a**-F⁻, **1a**-CN⁻,**1b**-F⁻, and **1b**-CN⁻ at B3LYP/6-31G(d,p) level (PCM = CH_2Cl_2).

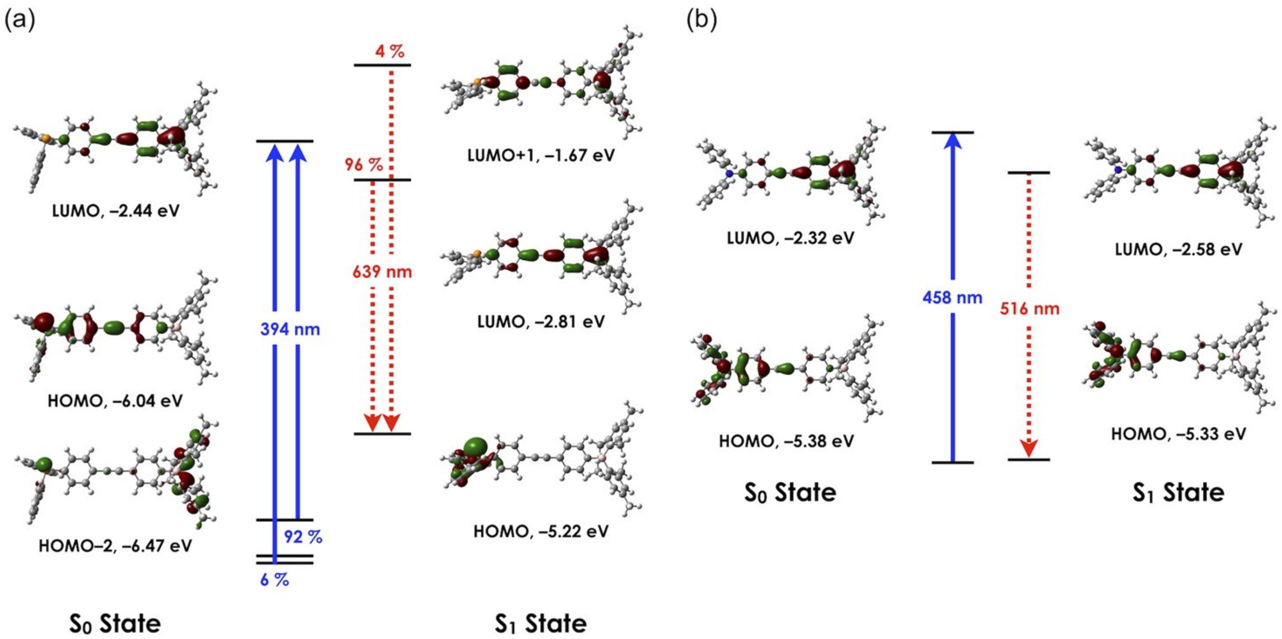


Fig. S8 Assignment of TD-DFT based absorption and fluorescence transitions of (a) **1a** and (b) **1b** calculated at B3LYP/6-311+G(d,p)//B3LYP/6-31G(d,p) level (PCM = CH_2Cl_2). In S_0 state, while the HOMO of **1b** is localized on the triphenylamine moiety, that of **1a** is localized on the phosphorus and phenylene phosphorus units. In contrast, the LUMO of **1a** and **1b** were similar. Therefore, the HOMO–LUMO gap of **1b** is smaller than that of **1a** because of the higher energy of the HOMO of **1b**.

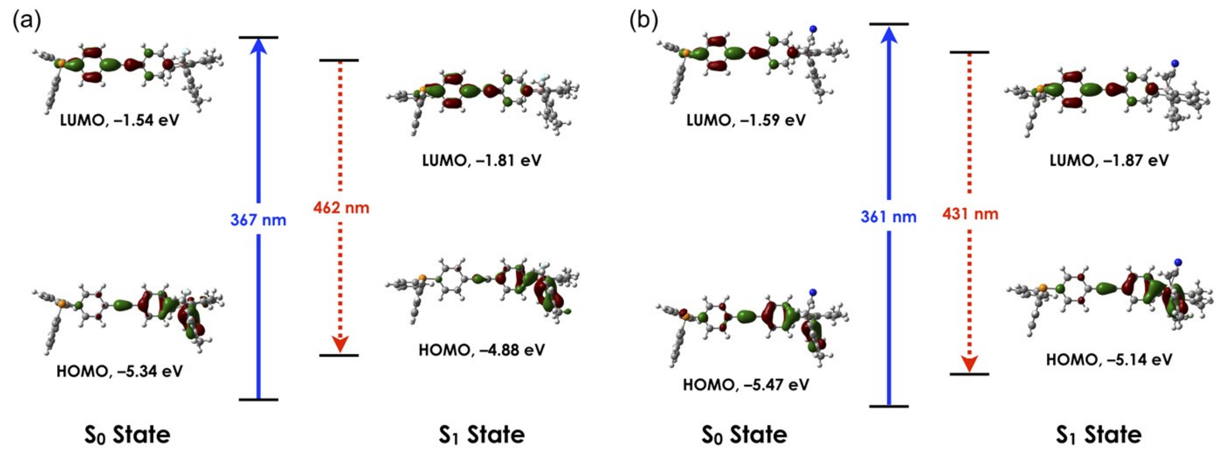


Fig. S9 Assignment of TD-DFT based absorption and fluorescence transitions of (a) **1a**–F⁻ and (b) **1a**–CN⁻ calculated at B3LYP/6-311+G(d,p)//B3LYP/6-31G(d,p) level (PCM = CH_2Cl_2).

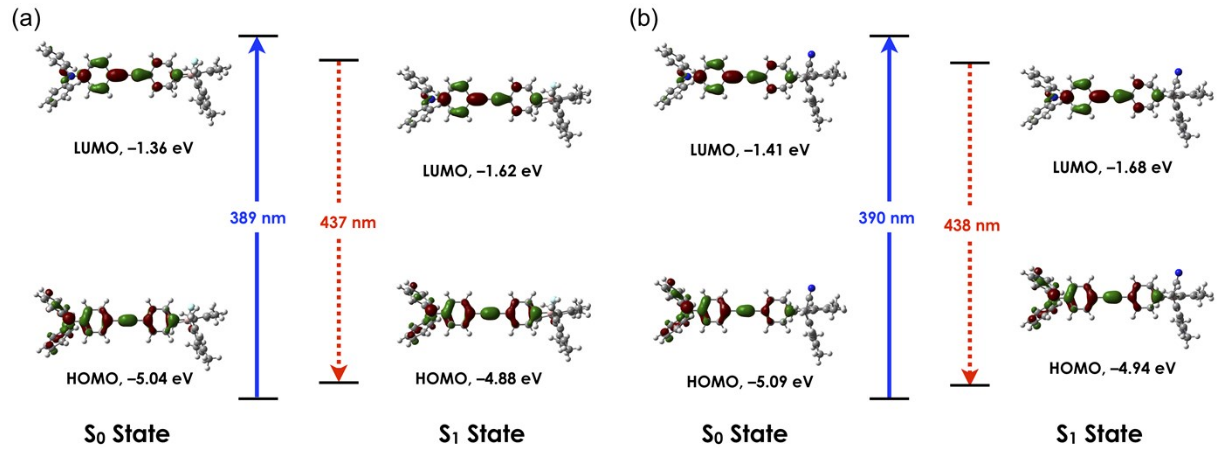


Fig. S10 Assignment of TD-DFT based absorption and fluorescence transitions of (a) **1b**–F⁻ and (b) **1b**–CN⁻ calculated at B3LYP/6-311+G(d,p)//B3LYP/6-31G(d,p) level (PCM = CH_2Cl_2).

Table S2 Summary of TD-DFT calculation at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d,p) level (PCM = CH_2Cl_2) for photophysical data.

	Absorption			Emission		
	Transition (*f*)	*E* (eV)	λ_{abs} (nm)	Transition (*f*)	*E* (eV)	λ_{em} (nm)
1a	$S_1 \leftarrow S_0$ (1.372)	3.144	394	$S_1 \rightarrow S_0$ (0.106)	1.941	639
1a–F⁻	$S_1 \leftarrow S_0$ (1.227)	3.374	367	$S_1 \rightarrow S_0$ (0.791)	2.681	462
1a–CN⁻	$S_1 \leftarrow S_0$ (1.499)	3.432	361	$S_1 \rightarrow S_0$ (1.260)	2.876	431
1b	$S_1 \leftarrow S_0$ (1.195)	2.706	458	$S_1 \rightarrow S_0$ (1.235)	2.405	516
1b–F⁻	$S_1 \leftarrow S_0$ (1.569)	3.186	389	$S_1 \rightarrow S_0$ (1.692)	2.835	437
1b–CN	$S_1 \leftarrow S_0$ (1.562)	3.181	390	$S_1 \rightarrow S_0$ (1.652)	2.827	438

Cartesian Coordination of 1a
B3LYP/6-31G(d,p)
–2067.0381622 hartree
C,-2.7372687617,0.4900899744,0.1144645696
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Cartesian Coordination of 1b

B3LYP/6-31G(d,p)

–1780.4381759 hartree

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H,4.2483160253,2.6530992584,1.0439264771
H,5.4854185865,1.4059569246,1.1435213851
H,5.8948271231,3.0157273346,0.5323630284
H,4.1157907232,0.8345250087,-4.569733214
H,2.5902428309,-1.4618697762,-2.2181881433
H,1.6330811796,-0.254107654,-3.0556771664
H,2.9505641199,-1.0695138336,-3.9015608109
C,5.9003695873,-2.8304806991,4.4218630825
C,5.8987724077,2.8936177944,-4.3829731537
H,5.3532418497,-3.7426928813,4.6919238807
H,6.9119358435,-3.1344575844,4.1352788896
H,5.9727614141,-2.2164711803,5.3244347562
H,5.9814558504,2.2800490567,-5.2849624929
H,5.3450534358,3.8008802706,-4.6562558484
H,6.9060488633,3.2066032381,-4.0910340379
N,-9.6292363458,-0.0337848437,-0.0198366795

Cartesian Coordination of 1a–F⁻

B3LYP/6-31G(d,p) (PCM = CH_2Cl_2)

–2167.0385932 hartree

C,0.7219472007,-0.1116940405,-0.8276047957
C,1.939488143,-0.151184619,-0.8716729144
C,3.3613759833,-0.187319845,-0.9274989492
C,4.1144472361,-0.7661086314,0.1148462797
C,4.0542292081,0.353326769,-2.0319009827
C,5.5050816226,-0.7936873124,0.0581545987
H,3.5974781687,-1.1895790997,0.9700928369
C,5.4422141949,0.3095806988,-2.0848430258
H,3.4910439611,0.7958504055,-2.8471652574
C,6.1957648883,-0.2523957434,-1.038192546
H,6.0571471004,-1.2428126774,0.8773065572
H,5.9500031182,0.7168759582,-2.9554821398
C,8.5381521076,1.3738815963,-0.5341157625
C,7.72722489,2.1661042709,0.2936324238
C,9.8099661991,1.8551227628,-0.8888810733
C,8.180984085,3.4016062979,0.7611815343
H,6.7367923759,1.8200889068,0.5717268426
C,10.267550673,3.0845467087,-0.4136872533
H,10.443916383,1.2647548303,-1.5457537654
C,9.4519487,3.8621860039,0.4116192056
H,7.5401200738,4.0035318485,1.3991320011
H,11.254582615,3.4393192818,-0.6959934122
H,9.8022894455,4.8239488708,0.77465136
C,8.5838000383,-1.4610515969,0.0686386172
C,8.8910422937,-1.1071087883,1.3917219885
C,8.7235656523,-2.8052600001,-0.3170567048
C,9.3174128219,-2.0735460544,2.3054787997
H,8.7999848929,-0.0735475875,1.7100520319
C,9.139723527,-3.7727268853,0.5981523866
H,8.5083874237,-3.0953292099,-1.3424134306
C,9.4400797663,-3.4078334488,1.9125164233
H,9.5525066406,-1.7827027086,3.325403652
H,9.2382353687,-4.8074045598,0.2828554992
H,9.7727987288,-4.1575577748,2.6243321382
C,-0.7002399898,-0.0548176895,-0.7800911519
C,-1.4305321568,0.6291681993,-1.7744290057
C,-1.4213918612,-0.6865084355,0.2552028506
C,-2.8196356737,0.6865835456,-1.7118195517
H,-0.8935530368,1.1078648706,-2.5892629974
C,-2.8106777604,-0.616246289,0.289668937
H,-0.8774990216,-1.2344473958,1.02010343
C,-3.5625458626,0.0895740532,-0.6719034573
H,-3.3625050358,1.2052931018,-2.4965628769
H,-3.3324327163,-1.1327296355,1.0919129019
B,-5.2123608157,0.1668812917,-0.6990142291
C,-5.7714796925,-1.337748642,-0.2411286393
C,-5.9454290249,1.4618832639,0.0698220104
C,-6.1600639143,-1.6720395153,1.0848107497
C,-5.7984769953,-2.4074397776,-1.1848371652
C,-7.3453767223,1.6460170969,-0.1500547798
C,-5.3120208397,2.4606459298,0.8581032729
C,-6.59782121,-2.9660970527,1.4144514084
C,-6.1301177808,-0.6762174094,2.2324477314
C,-6.2457861776,-3.6857639862,-0.8221841733
C,-5.3164917214,-2.2543750622,-2.617892512
C,-8.0352874933,2.7412668237,0.3858207465
C,-8.1772850152,0.6658957304,-0.9579978333
C,-6.035948046,3.5483498388,1.3793182958
C,-3.8363382648,2.4398712756,1.2172468526
C,-6.6678591631,-3.9909939861,0.4731969726
H,-6.8869904358,-3.175281594,2.4439533652
H,-5.2079399231,-0.0912444202,2.2530433731
H,-6.9509797701,0.0451222022,2.1719747676
H,-6.2162323224,-1.1996302371,3.1909300102
H,-6.2509900944,-4.4724752167,-1.5763659969
H,-5.9638220466,-1.5994477609,-3.2046577524
H,-4.3201580659,-1.8051835304,-2.6588515201
H,-5.2719499037,-3.2325705474,-3.1087955625
C,-7.39999442,3.7167258853,1.1566735389
H,-9.1039320379,2.8336234201,0.1934333622
H,-7.7517754313,0.519046621,-1.9513030826
H,-8.2047920477,-0.3207369444,-0.4844954336
H,-9.2077045544,1.0225670724,-1.0581489201
H,-5.5074460326,4.287490368,1.980262276
H,-3.5490262013,1.5284265433,1.7494856181
H,-3.1929119359,2.4912890661,0.3352857398
H,-3.591448855,3.2907609685,1.8614387028
C,-7.1782840584,-5.3671777338,0.8340733181
C,-8.1536780347,4.9092612562,1.6989134614
H,-6.631042844,-6.1524201421,0.3012674527
H,-7.0850920407,-5.5600508346,1.9076758287

H,-8.2387960178,-5.4867122737,0.5753305908
H,-7.6199871419,5.3745375836,2.5337270612
H,-8.2932838433,5.6827773784,0.9321737954
H,-9.1523657676,4.6284632841,2.0512401498
F,-5.5416541517,0.3975823984,-2.1132971978
P,8.0355924424,-0.2661035615,-1.237366896

Cartesian Coordination of 1a–CN⁻
B3LYP/6-31G(d,p) (PCM = CH_2Cl_2)
–2160.0134297 hartree
C,0.5263750312,-0.0057447658,0.843550566
C,1.7440179854,0.0409232568,0.8575597161
C,3.1666625681,0.0947183581,0.8716436376
C,3.8767941313,0.7141815826,-0.17705302
C,3.9016257121,-0.4649567546,1.9384066747
C,5.2678588185,0.7642195084,-0.1624084784
H,3.3263491845,1.1520030276,-1.0036727043
C,5.289765066,-0.398757809,1.9498102996
H,3.3714000963,-0.9394887431,2.7577127378
C,6.0008079687,0.2053649884,0.8968219832
H,5.7867385648,1.2445526264,-0.9853986509
H,5.8310213036,-0.8217454049,2.7923287611
C,8.3512980234,-1.3811829877,0.322750754
C,7.5256279584,-2.1863941674,-0.4774186812
C,9.6420903102,-1.8416856487,0.6338744265
C,7.9832393627,-3.414434629,-0.9605335732
H,6.5211794407,-1.8559585649,-0.7220878832
C,10.1031847523,-3.0635376313,0.1427767857
H,10.2885459893,-1.2409815592,1.2687839296
C,9.2727265295,-3.8543233616,-0.6547314342
H,7.3310506057,-4.0266074106,-1.5768822562
H,11.1049270517,-3.4020334309,0.3911449401
H,9.6260873621,-4.8101965097,-1.0301280972
C,8.3323602345,1.4528856326,-0.2843301809
C,8.6044797747,1.1002579518,-1.6154247869
C,8.4591631784,2.8006529992,0.0934603699
C,8.9843491625,2.0713440924,-2.544582216
H,8.5215483634,0.0643018001,-1.9280667033
C,8.8280596859,3.7726647955,-0.8371122679
H,8.2706514181,3.0899857329,1.124247666
C,9.0940304002,3.4089965137,-2.1591943727
H,9.1928509067,1.781638402,-3.5705733321
H,8.9170001702,4.8100576049,-0.5279948221
H,9.3900527291,4.1625153223,-2.8831048859
C,-0.896883871,-0.0575714217,0.8255373677
C,-1.6138531299,-0.7374153253,1.8303443207
C,-1.6347320391,0.5823389699,-0.1912606472
C,-3.0051314954,-0.7779395247,1.800378686
H,-1.0684078089,-1.2278948479,2.6318594487
C,-3.0252322596,0.5331674752,-0.1922593301
H,-1.1046147965,1.1237600137,-0.9699678665
C,-3.7686179771,-0.1603404802,0.7864616254
H,-3.5188180606,-1.3081281719,2.5977150133
H,-3.5539955709,1.0607715396,-0.9804398521
B,-5.4297739224,-0.1715303129,0.769566136
C,-5.9034120926,1.3318207256,0.2182233538
C,-6.2157654504,-1.4683133807,0.0343437033
C,-6.2421060248,1.5731440004,-1.1448458037
C,-5.881716808,2.4801002982,1.062804683
C,-7.6435406103,-1.5217575343,0.0990572853
C,-5.5850907255,-2.5735039712,-0.602370291
C,-6.6186601584,2.8527041087,-1.5843350155
C,-6.2048052819,0.5032335982,-2.2233411448
C,-6.2693263867,3.7416047818,0.5879592859
C,-5.4084883562,2.4384023915,2.504268304
C,-8.3588008804,-2.6023306755,-0.4349144581
C,-8.4877236656,-0.4226126309,0.7200377993
C,-6.3398838498,-3.6388155988,-1.1235606417
C,-4.0852728634,-2.6974301689,-0.8040618838
C,-6.6671466079,3.9537968741,-0.7315738767
H,-6.8717758081,2.9889511354,-2.6350000313
H,-5.3317551624,-0.1461668575,-2.135753649
H,-7.0818307749,-0.1504507869,-2.1889277987
H,-6.1782444626,0.9715899187,-3.2129826179
H,-6.2426745299,4.5880710115,1.273015839
H,-6.1442279862,1.9844248134,3.1744717925
H,-4.4887032949,1.8575850729,2.6131106968
H,-5.2102789336,3.4526807986,2.8653150794
C,-7.7293278601,-3.6845586568,-1.0497723938
H,-9.4458243864,-2.5936979118,-0.3667092573
H,-8.2370979896,-0.2562730834,1.7708699672
H,-8.3478385814,0.5345084319,0.2106762237
H,-9.5494071631,-0.6830215934,0.6664539725
H,-5.8135294634,-4.4601739674,-1.6076547908
H,-3.6628102519,-1.836940619,-1.3292236339
H,-3.5408158257,-2.7760573946,0.1403083471
H,-3.8588567227,-3.5915570758,-1.3934908109
C,-7.1195671209,5.3121074492,-1.2145190232
C,-8.5164701933,-4.8567693831,-1.5877515348
H,-6.6083334332,6.1193988574,-0.6798644955
H,-6.9294850283,5.4409981023,-2.2849265657
H,-8.1968500902,5.45659555,-1.0591919416
H,-7.9517534465,-5.4017288799,-2.3507475272
H,-8.7646853078,-5.574041249,-0.7944549292
H,-9.4637256542,-4.5345558328,-2.0332937014
P,7.8457373712,0.2515363976,1.0401507906
C,-5.8527643023,-0.4384441524,2.3131411254
N,-6.1265972443,-0.7512470138,3.4048524255

Cartesian Coordination of 1b–F⁻
B3LYP/6-31G(d,p) (PCM = CH_2Cl_2)
–1880.436935 hartree
C,0.602952428,0.059498019,-0.4413611071
C,1.8175360457,0.0297709672,-0.3393136081
C,3.2348939125,-0.0018319704,-0.2137807138
C,3.8567763864,-0.7116206167,0.8354269811
C,4.0647793632,0.678110335,-1.1303730735
C,5.2386802493,-0.7311882369,0.9683930335
H,3.2406628172,-1.236380783,1.5584960066
C,5.4474137105,0.645636918,-1.0072999577
H,3.6118890117,1.2228185563,-1.9525660588
C,6.0592252416,-0.0547030585,0.047968761
H,5.6918565349,-1.2710897726,1.7926647947
H,6.0637927921,1.1650435037,-1.7329756564
C,8.2362391758,1.0898103429,-0.0862042453
C,7.7959236566,2.3494424131,0.3523980776
C,9.4485706252,0.9993456206,-0.7895663392
C,8.5495595048,3.4905883716,0.0826652151
H,6.8649182102,2.4283908056,0.9034786037
C,10.2046132225,2.1437789823,-1.038000049

H,9.7923467235,0.0313917871,-1.1384090072
C,9.7598651151,3.3965293266,-0.6087542934
H,8.1936310133,4.4564265245,0.4294385109
H,11.1396295932,2.0549061674,-1.5836024835
H,10.3475274857,4.286673025,-0.8104382151
C,8.1260875712,-1.2720330436,0.5968790778
C,9.1522353093,-1.2235856484,1.5542352079
C,7.7580131932,-2.5136798975,0.0538197644
C,9.7992165106,-2.3930613922,1.9505871644
H,9.4373498111,-0.2690070569,1.9836725895
C,8.3982339614,-3.6800224439,0.4696840582
H,6.9714714419,-2.5584017408,-0.6920564828
C,9.4245212402,-3.6281632312,1.416135939
H,10.5907508204,-2.3377758874,2.6923563759
H,8.1010909896,-4.632028198,0.0394594443
H,9.9255064218,-4.5377358509,1.7325554527
C,-0.8172636077,0.099534945,-0.5480376349
C,-1.4514633384,0.8323582362,-1.5731108739
C,-1.6334738317,-0.5991566236,0.3663461833
C,-2.8408016466,0.870658653,-1.6550219885
H,-0.8405698358,1.363896799,-2.2983363328
C,-3.0200112976,-0.5441342673,0.2589231137
H,-1.1641978795,-1.1856072313,1.1519410517
C,-3.679281634,0.2077842695,-0.7346046329
H,-3.3054970879,1.4282108838,-2.4633060743
H,-3.6138104625,-1.1111905593,0.9719330816
B,-5.3189282444,0.2695064221,-0.9281300499
C,-5.9068533035,-1.2516598647,-0.5720676931
C,-6.1422655037,1.5366107859,-0.2028881087
C,-6.4190019475,-1.6264195839,0.7006316227
C,-5.8290765088,-2.2945800475,-1.5419616251
C,-7.5115367472,1.7206436615,-0.5677732646
C,-5.6061478888,2.51403605,0.6786007525
C,-6.8696226841,-2.9332900252,0.9516700283
C,-6.5102968854,-0.6623027305,1.8716901495
C,-6.2933359497,-3.5871567865,-1.258638846
C,-5.2155144887,-2.0958753257,-2.9179218864
C,-8.2635582771,2.7976249192,-0.0811492191
C,-8.2434768146,0.7586993214,-1.4865596213
C,-6.3900257061,3.5843121869,1.1465750668
C,-4.1795385731,2.487032058,1.1989720795
C,-6.8344890586,-3.9325703445,-0.0191678883
H,-7.2534241089,-3.1744410634,1.9425991691
H,-5.5909249586,-0.0885551396,2.0106386595
H,-7.3131501787,0.0694428248,1.7404260126
H,-6.7056316583,-1.2103720127,2.7997922605
H,-6.2157912666,-4.3527157217,-2.0303166657
H,-5.8249158437,-1.4497725604,-3.5537309657
H,-4.2356830632,-1.6149819557,-2.854097852
H,-5.0928543064,-3.0613707663,-3.4206376158
C,-7.7222209655,3.7546153248,0.7795012983
H,-9.3058743421,2.8899851698,-0.3854739369
H,-7.718993149,0.6525269967,-2.4368253764
H,-8.3004416767,-0.2441923573,-1.0513783127
H,-9.2647398695,1.1049277564,-1.6768210236
H,-5.9361327771,4.3076712221,1.8231233108
H,-3.9340066497,1.5445916764,1.6956770781
H,-3.4431527071,2.6093920516,0.4002587652
H,-4.0252186112,3.2943198404,1.9224725288
C,-7.3611969362,-5.3226693615,0.2541381779
C,-8.5380537737,4.9295938092,1.2674631765
H,-6.7935886564,-6.0828162617,-0.2931639412
H,-7.3127322147,-5.5674167592,1.3202290899
H,-8.4107853446,-5.4257446916,-0.0521508787
H,-8.1005899123,5.3750640711,2.1666035295
H,-8.5993403527,5.7222745383,0.5100584568
H,-9.567088893,4.6361143096,1.5027647351
N,7.4700118028,-0.0788834951,0.1810524137
F,-5.5037167338,0.5402930564,-2.3613031707

Cartesian Coordination of 1b–CN⁻

B3LYP/6-31G(d,p) (PCM = CH_2Cl_2)

–1873.4119854 hartree

C,0.7377699483,0.0640420142,-0.4019991587
C,1.953438446,0.0514102199,-0.313495126
C,3.3731110932,0.0412200253,-0.2122519334
C,4.0293172617,-0.738150371,0.7638667539
C,4.1704322715,0.8125842511,-1.0841933498
C,5.4137212723,-0.7396040287,0.8688756832
H,3.4384777181,-1.3333502178,1.4526593598
C,5.5554280063,0.800089181,-0.989545499
H,3.6903029779,1.4132706096,-1.849962037
C,6.2022985415,0.0270610579,-0.0082395956
H,5.893673721,-1.3358756024,1.6371377892
H,6.1466052351,1.390934451,-1.680578726
C,8.3528471675,1.2211963657,-0.1112811078
C,7.9153492505,2.4325250562,0.4486146179
C,9.5320318955,1.2087025442,-0.8736165011
C,8.6389483182,3.6053239105,0.2387701993
H,7.010043059,2.4489126578,1.0461547274
C,10.2589140177,2.3831038476,-1.0626583283
H,9.8726934084,0.2780283287,-1.3148784732
C,9.816317412,3.5887351037,-0.5130647558
H,8.2862917353,4.5335687882,0.6788766129
H,11.1686653367,2.3558943308,-1.6554342638
H,10.3809547709,4.5027444648,-0.6684900974
C,8.3058613611,-1.1846785692,0.4025436342
C,9.363598127,-1.1814821702,1.3261220425
C,7.9434288905,-2.3925576117,-0.2153690873
C,10.0467999885,-2.3615472926,1.6159498598
H,9.6448051157,-0.2534467278,1.8125320777
C,8.6203216412,-3.5710357267,0.094699733
H,7.132961498,-2.4017487652,-0.9364432831
C,9.6780586534,-3.5636657225,1.0073363826
H,10.8625852968,-2.341425214,2.332799806
H,8.3270516166,-4.4964799211,-0.3923754467
H,10.2075913968,-4.4820552285,1.2408927089
C,-0.6834314297,0.0865513766,-0.5009582253
C,-1.3318913747,0.8511970656,-1.4919146482
C,-1.4882303892,-0.6602863829,0.383269806
C,-2.721481839,0.8710332383,-1.5727547258
H,-0.7339378498,1.4247590899,-2.1948769009
C,-2.8757562918,-0.6265994718,0.2766596002
H,-1.0120321968,-1.2686411578,1.1474045246
C,-3.551465232,0.151189142,-0.6869393923
H,-3.1798288445,1.4692483979,-2.3558438489
H,-3.4568099928,-1.2311207537,0.967100642
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[S4 (Complete form of ref. 13 in the manuscript)] Gaussian 16 (Revision A.03), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[S5] a) B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *106*, 5151–5158; b) E. CancHs, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, 107, 3032–3041; c) M. Cossi, V. Barone, B. Mennucci, J. Tomasi, *Chem. Phys. Lett.* **1998**, *286*, 253–260.

4. Ion-binding properties

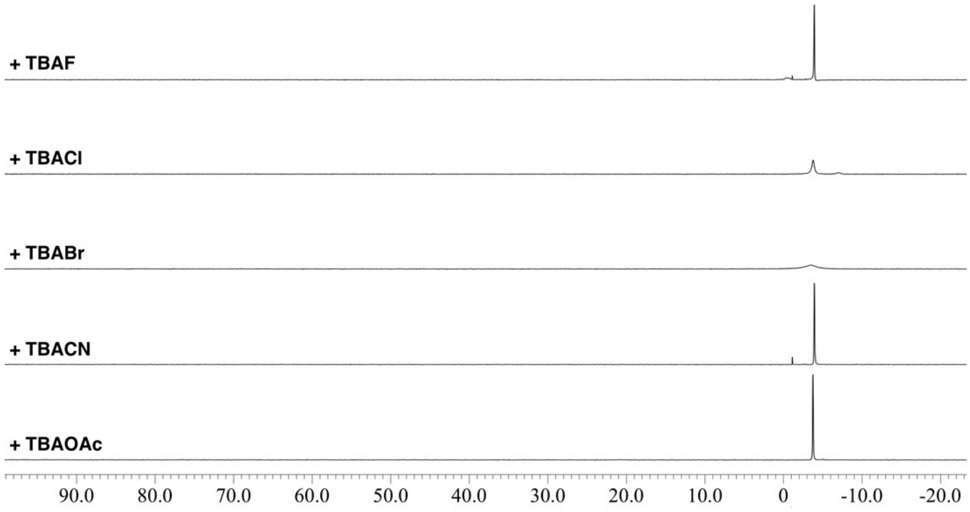

Fig. S11 ^{11}B NMR spectral changes of tris(pentafluorophenyl)borane (5.5 mM) upon the addition of F^-, Cl^-, Br^-, AcO^- and CN^- as TBA salts (10 equiv) in CH_2Cl_2. The chemical shifts of the boron–anion complexes were appeared at –3.9, –3.8, –3.4, –3.9, and –3.8 ppm for F^-, Cl^-, Br^-, CN^-, and AcO^-, respectively, whereas that of tris(pentafluorophenyl)borane was at 62 ppm,[S5] indicating the formation of pyramidal four-coordinate boron centres.

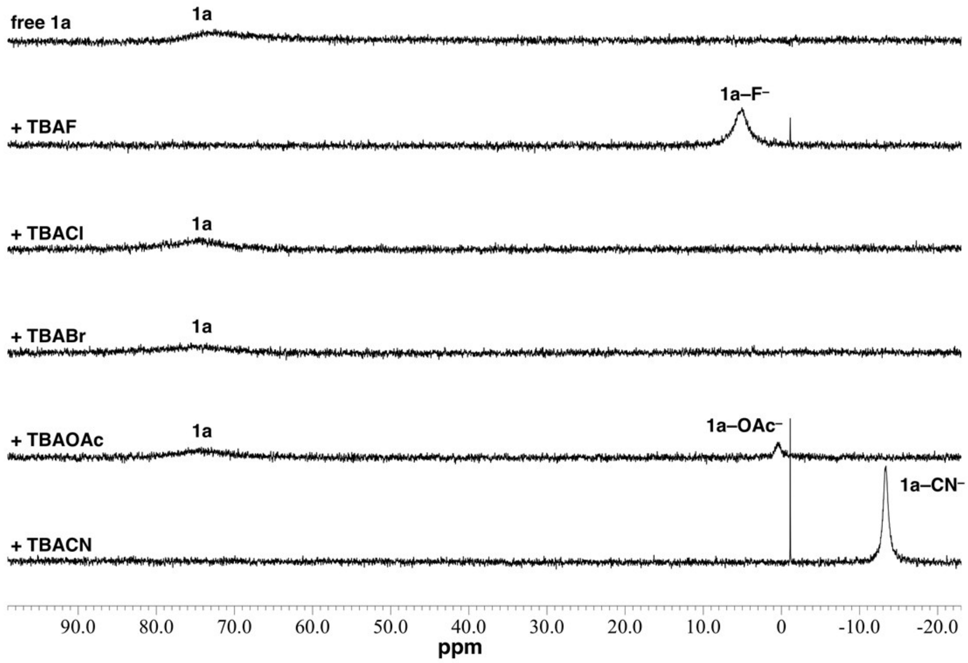

Fig. S12 ^{11}B NMR spectral changes of **1a** (5.5 mM) upon the addition of F^-, Cl^-, Br^-, AcO^- and CN^- as TBA salts (10 equiv) in CH_2Cl_2. An unknown signal at –1.1 ppm, which observed with the addition of TBAF or TBACN, was probably derived from the complex with OH^- generated by H_2O with F^- or CN^- as the base, because the similar signal was observed by the addition of TBAOH.

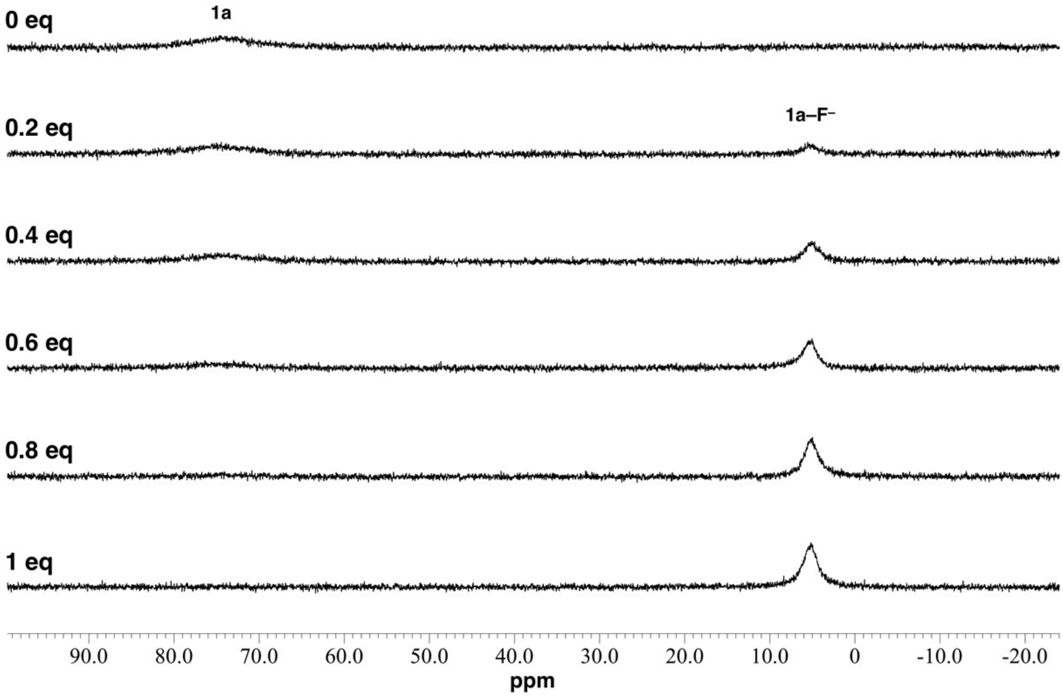

Fig. S13 ^{11}B NMR spectral changes of **1a** (5.5 mM) upon the addition of F^- as TBA salt (0~1 equiv) in CH_2Cl_2. The signals of **1a**–F^- appeared at 5.04 ppm, whereas the signal of the free **1a** at 73 ppm decreased.

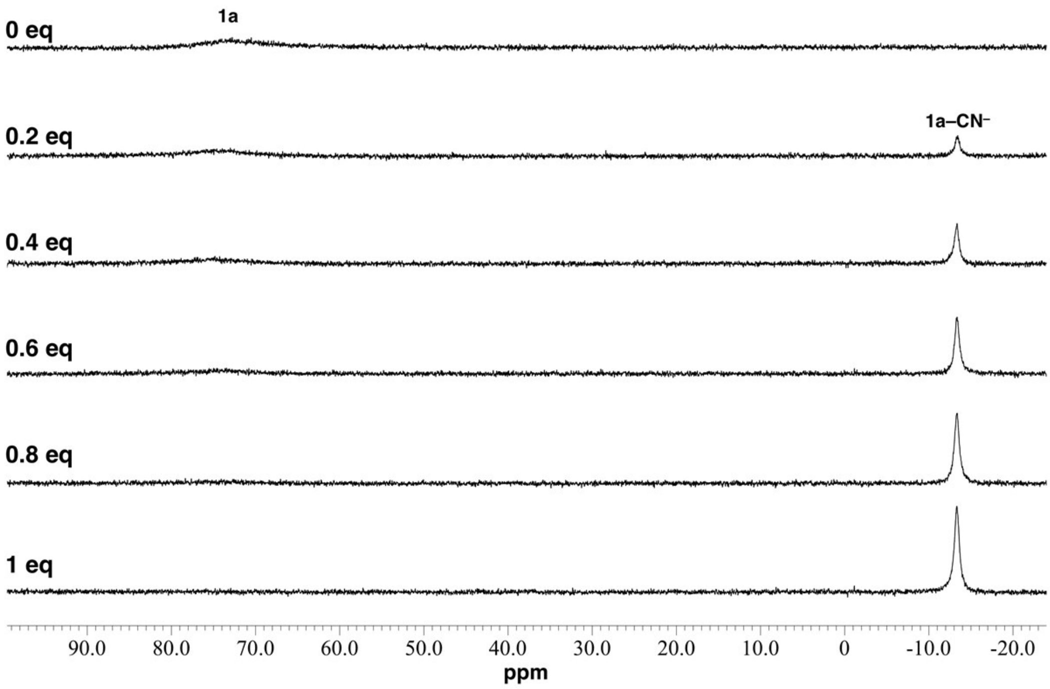

Fig. S14 ^{11}B NMR spectral changes of **1a** (5.5 mM) upon the addition of CN^- as TBA salt (0~1 equiv) in CH_2Cl_2. The signals of **1a**–CN^- appeared at –13.38 ppm, whereas the signal of the free **1a** at 73 ppm decreased.

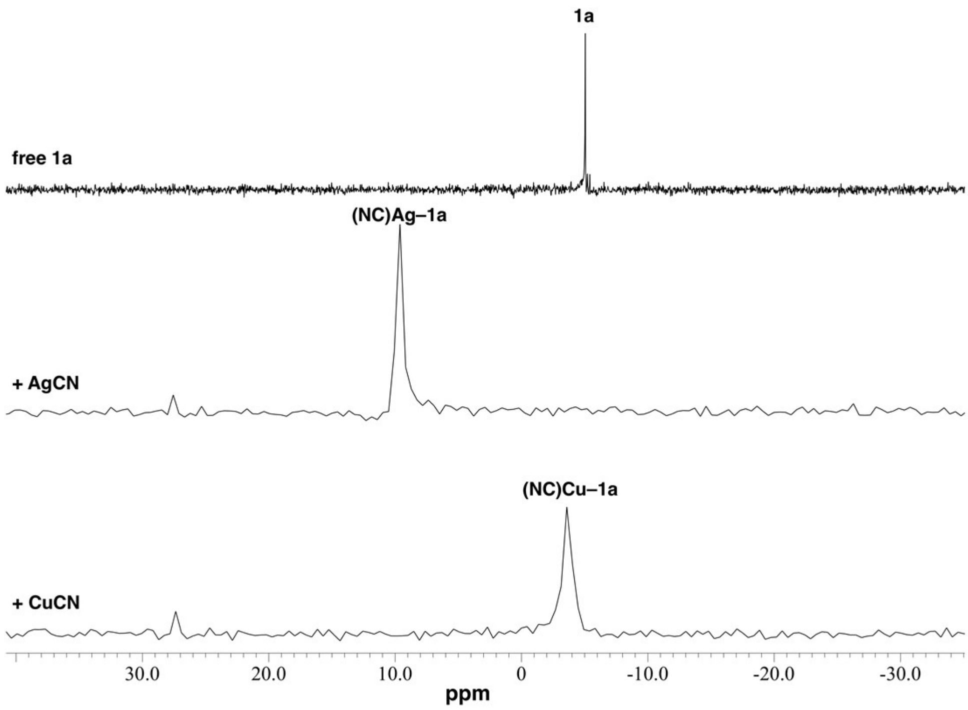

Fig. S15 ^{31}P NMR spectral changes of **1a** (5.5 mM) upon the addition of AgCN and CuCN (1 equiv.) in CH_2Cl_2.

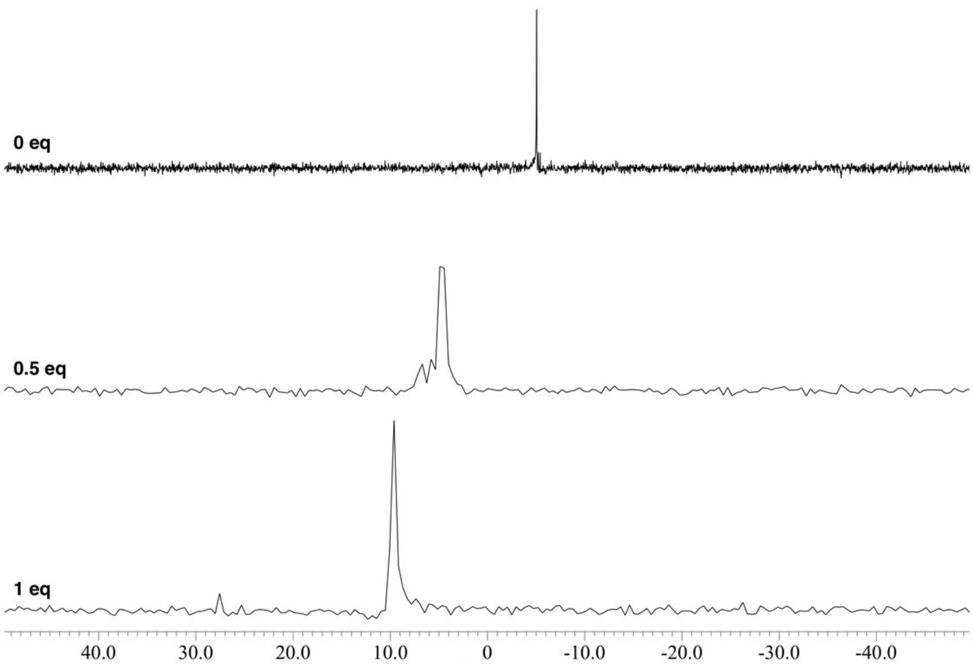

Fig. S16 ^{31}P NMR spectral changes of **1a** (5.5 mM) upon the addition of AgCN (0.5, 1 equiv.) in CH_2Cl_2.

Table S3 Summary of ^{11}B NMR chemical shift (δ, ppm) data of **1a** with various anions in CH_2Cl_2.

	free	F^-	AcO^-	CN^-
1a	73.24	5.04	–0.53	–13.38

Table S4 Summary of ^{31}P NMR chemical shift (δ, ppm) data of **1a** with various ion pairs in CH_2Cl_2.

	free	AgCN	CuCN	AgCN+TBACN	CuCN+TBACN
1a	–5.05	9.62	–3.59	–2.05	–5.38

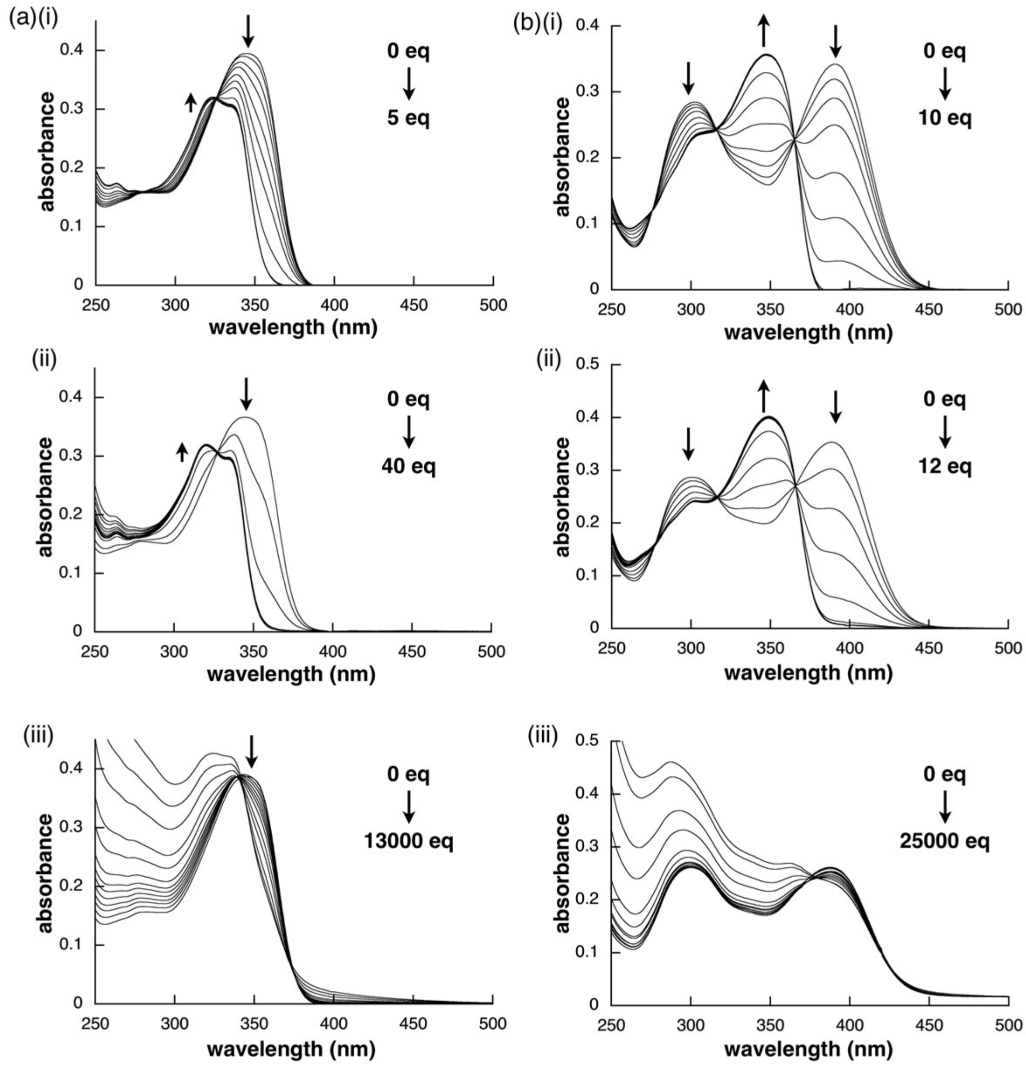

Fig. S17 UV/vis absorption spectral changes of (a) **1a** and (b) **1b** upon the addition of (i) F^-, (ii) CN^- and (iii) AcO^- as TBA salts in CH_2Cl_2 (10^{-5} M).

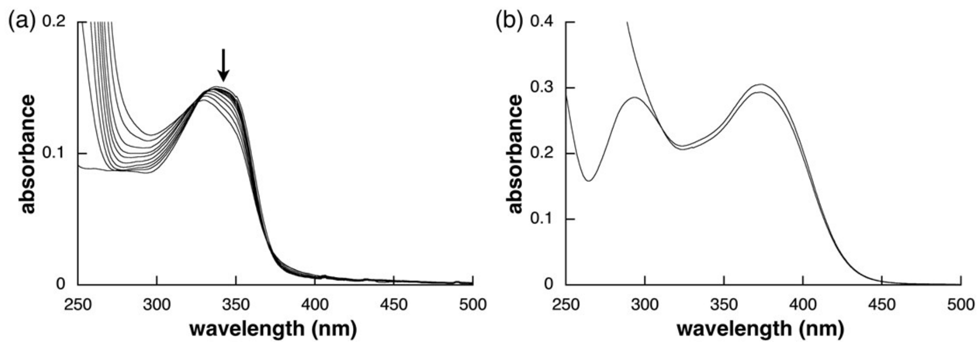

Fig. S18 UV/vis absorption spectral changes of (a) **1a** and (b) **1b**, upon the addition of CuI in CH_3CN (5×10^{-6} M for **1a** and 10^{-5} M for **1b**).

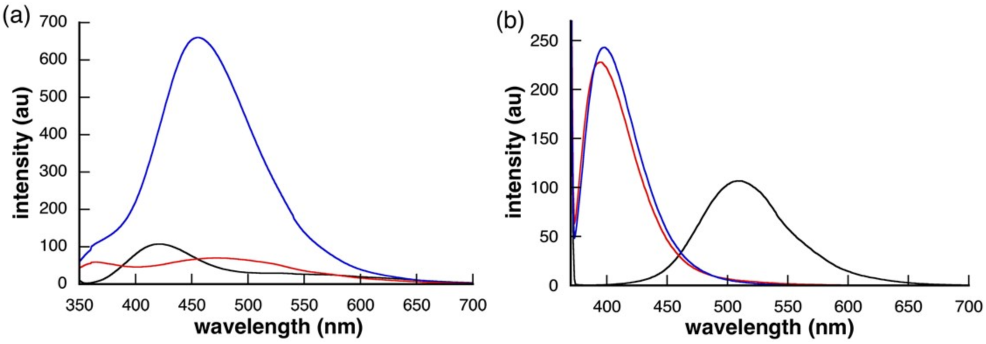

Fig. S19 Emission spectra of (a) **1a** and (b) **1b** without ion pair (black), with 3 eq of TBAF (red) and with 3 eq of TBACN (blue) in CH_2Cl_2 (10^{-5} M). The fluorescence spectra were obtained by excitation at respective isosbestic points of anion titration. See Fig. S16.

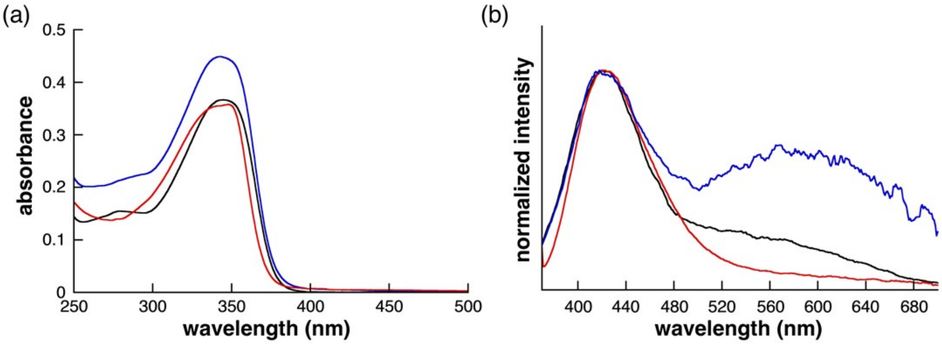

Fig. S20 (a) UV/vis absorption and (b) emission spectral changes of **1a** (black) upon the addition of AgCN (red) and CuCN (blue) in CH_2Cl_2. (0.01 mM)

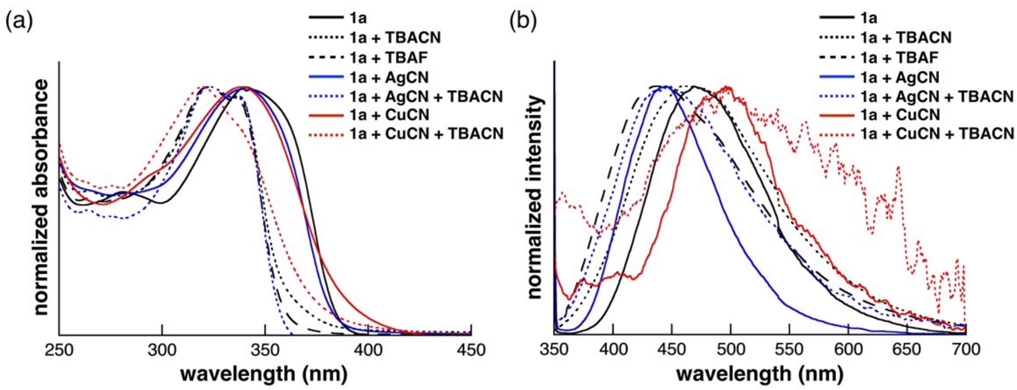

Fig. S21 (a) UV/vis absorption and (b) emission spectral changes of **1a** (solid line, black) upon the addition TBACN (1 eq, dotted line, black), TBAF (1 eq, dashed line, black) AgCN (1 eq, solid line, blue), CuCN (1 eq, solid line, red), TBACN/AgCN (1 eq, dotted line, blue) and TBACN/CuCN (1 eq, dotted line, red) in film state.

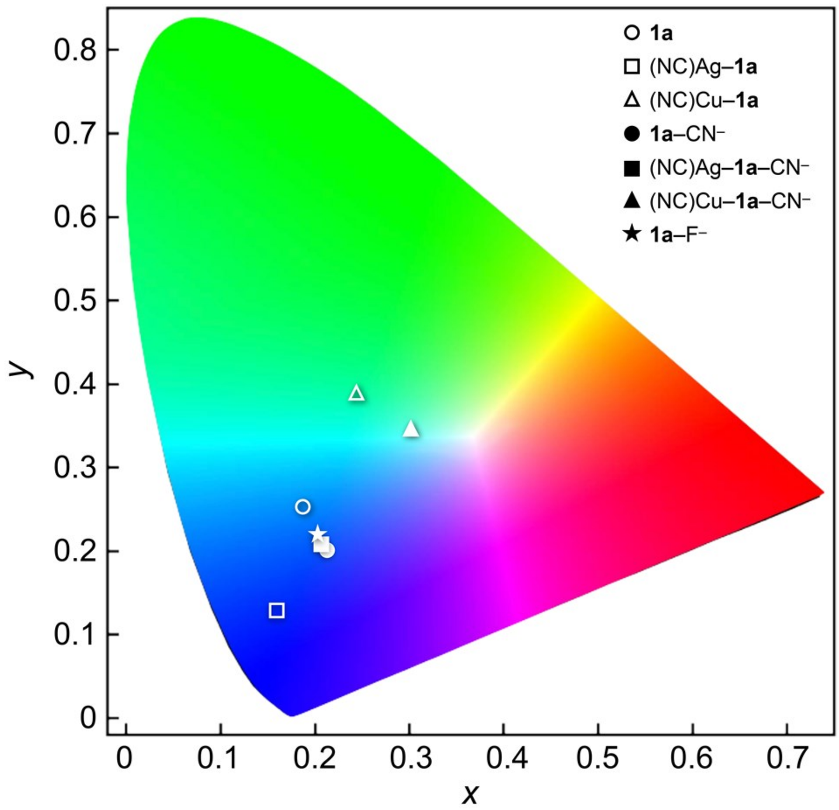

Fig. S22 Emission colour coordinates of **1a** with various ion pairs in the CIE 1931 chromaticity diagram.

Table S5 Summary of emission colour coordinates of **1a** with various ion pairs in the CIE 1931 chromaticity diagram.

	In CH_2Cl_2	Film
1a	(0.205, 0.210)	(0.186, 0.255)
1a–F^-	(0.211, 0.278)	(0.202, 0.224)
1a–CN^-	(0.177, 0.209)	(0.212, 0.203)
(NC)Ag–**1a**	–	(0.158, 0.130)
(NC)Ag–**1a**–CN^-	–	(0.197, 0.218)
(NC)Cu–**1a**	–	(0.243, 0.389)
(NC)Cu–**1a**–CN^-	–	(0.299, 0.346)

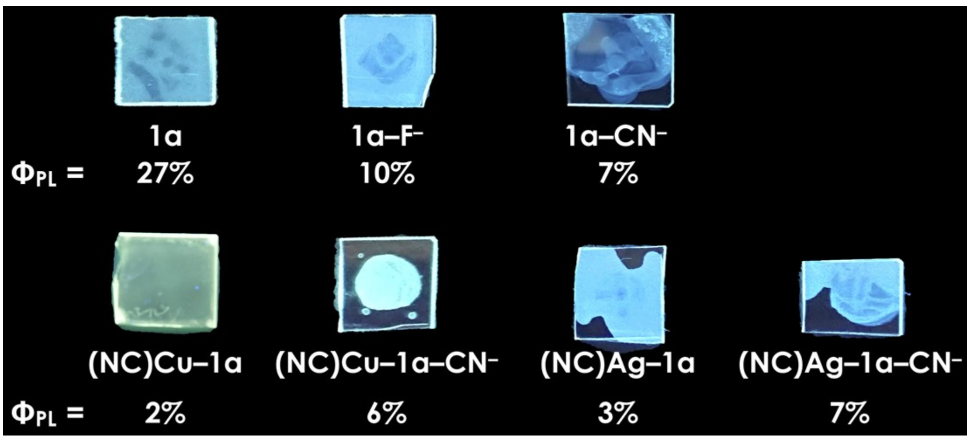

Fig. S23 Photographs of **1a** with various ion pairs under UV irradiation.

[S5] S. Mitu and M. C. Baird, *Organometallics*, 2006, **25**, 4888-4896.