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Electronic Supplementary Information

Interlocked dimerization of C_3-Symmetrical Boron Difluoride Complex: Designing Non-Cooperative Supramolecular Materials for Luminescent Thin Films

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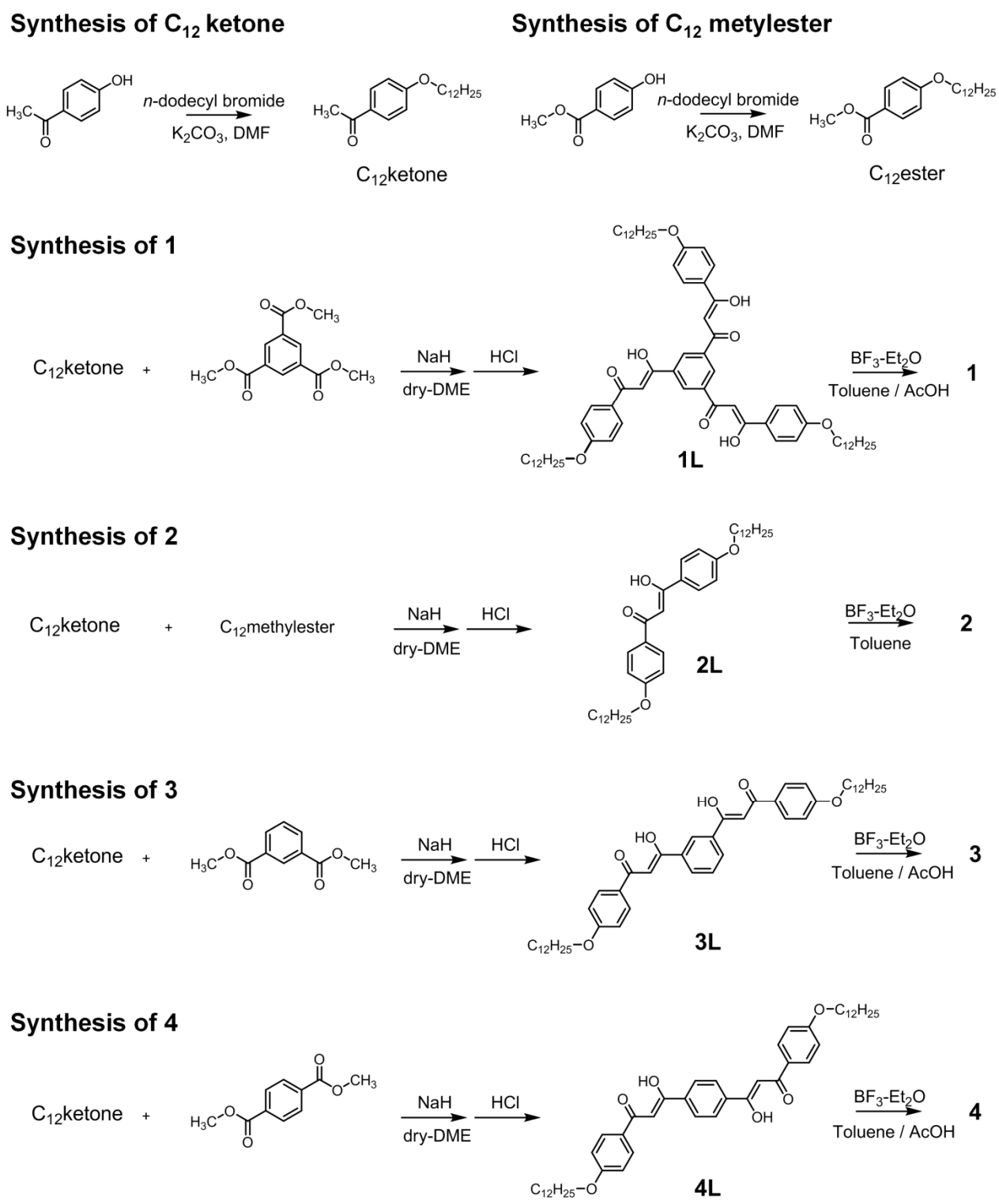
1. Supplementary Methods

General procedures. Anhydrous *N*,*N*-dimethylformamide (DMF) was obtained by using Solvent Dispensing System of Glass Contour (Nikko Hansen & Co., Ltd.). Toluene and acetic acid were distilled from phosphorus pentoxide and excess acetic anhydride, respectively. All other chemicals were purchased from commercial sources and used without further purification. The purities of products were analyzed by using 300 MHz ^{1}H-NMR spectroscopy (AVANCE 300 M Type NMR, Bruker BioSpin Co., Ltd.), MALDI-TOF-MS analysis (autoflex III TOF/TOF, Bruker Daltonics Co., Ltd.), FT-IR spectroscopy (FT-IR-8400S, SHIMADZU Corp.) and elemental analysis (YANACO CHN corder MT-5 and MT-6, Yanaco New Science Inc.). In ^{1}H-NMR measurements, chemical shifts δ are listed relative to tetramethylsilane (TMS: 0 ppm) and chloroform (7.26 ppm), and representative coupling constants J are in hertz. Melting points of synthetic compounds were obtained by using MP-500D (Yanaco New Science Inc.). Thermogravimetry was recorded on TG/DTA 320 (SII Nano Technology Inc.) and decomposition temperatures (d.p.) were determined under N_2 atmosphere.

Synthetic procedures. The synthetic routes for compounds **1L**–**4L** and **1**–**4** were shown in Scheme S1. Four types of *β*-diketonate ligands **1L**–**4L** were prepared through a standard Claisen condensation between *para*-dodecanoxyacetophenone and corresponding methylester materials with sodium hydride in anhydrous dimethoxyethane (DME). Their ligands were further reacted with BF_3•Et_2O in mixed solvent of toluene/acetic acid or toluene solely to afford **1**–**4**. The synthesis and purification of **3L**, **3**, **4L**, **4** were reported in reference 10b.



Scheme S1. Synthetic routes of lipophilic boron difluoride *β*-diketonate (BF_2dk) complexes (**1**–**4**) and the corresponding ligands (**1L**–**4L**).

***para*-Dodecyloxyacetophenone (C_{12}ketone)**. Anhydrous potassium carbonate (29.0 g, 210 mmol) was dispersed in anhydrous DMF (110 mL) and stirred under N_2 atmosphere for 1 hr. It was further degassed by ultrasonication for 5 mins, and then *p*-hydroxyacetophenone (9.9 g, 72.7 mmol) and 1-bromododecane

(18.1 g, 72.7 mmol) were added to the solution. The solution was stirred for 6.5 hrs at 65 ºC. After the reaction mixture was cooled to room temperature, it was poured into 300 mL water in ice bath. The obtained precipitates were recrystallized from acetone/water to afford product as white powder with m.p. 47.6 – 47.8 °C. Yield: 21.1 g, 95.4 %. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.92 (d, 2H, 8.73 Hz), 6.92 (d, 2H, 8.73 Hz), 4.01 (t, 2H), 2.55 (s, 3H), 1.8 (quintet, 2H), 1.2-1.5 (m, 18H), 0.88 (t, 3H). MS (MALDI-TOF, *m/z*), cal: 304.2, found: 305.1 $[M+H]^+$. Elemental Analysis: CHN cal: 78.90% C, 10.59% H. Found: 78.87% C, 10.60% H. IR (ATR / cm^{-1}) 2920, 2850, 1676, 1605, 1580, 1508, 818.

Methyl-*para*-dodecyloxy benzoate (C_{12}methylester). Anhydrous potassium carbonate (28.0 g, 203 mmol) was dispersed in anhydrous DMF (110 mL) and stirred under N_2 atmosphere for 1 hr. It was further degassed by ultrasonication for 5 mins, and then methyl-*p*-hydroxy benzoate (10.0 g, 65.7 mmol) and 1-bromododecane (16.7 g, 67.0 mmol) were added to the solution. The solution was stirred for 6.5 hrs at 65 ºC. After the reaction mixture was cooled to room temperature, it was poured into 300 mL water in ice bath. The obtained precipitates were recrystallized from acetone/water to afford product as white powder with m.p. 54.7 – 54.9 °C. Yield: 20.6 g, 97.9 %. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.98 (d, 2H, 8.78 Hz), 6.9 (d, 2H, 8.78 Hz), 4.0 (t, 2H), 3.88 (s, 3H), 1.8 (quintet, 2H), 1.2-1.5 (m, 18H), 0.88 (t, 3H). MS (MALDI-TOF, *m/z*), cal: 320.2, found: 318.9 $[M-H]^+$. Elemental Analysis: CHN cal: 74.96% C, 10.06% H. Found: 74.98% C, 10.04% H. IR (ATR / cm^{-1}) 2916, 2849, 1722, 1608, 1510, 1254, 835.

Ligand 1L. 60% NaH (2.52 g, 63 mmol) was added to round flask and atmosphere was substituted to nitrogen. Anhydrous DME (60 ml) solution containing trimethylbenzene-1,3,5-tricarboxylate (1.0 g, 4.0 mmol) and *para*-dodecanoxyacetophenone (4.35 g, 14.3 mmol) were poured into the flask in ice bath. The solution was stirred at 80 ºC for 10.5 hrs. After the reaction mixture was cooled to room temperature, it was poured into ice water (400 ml). 2.5 N HCl aq. was added to neutralize excess NaH. The mixture was extracted with chloroform, and the organic phase was dried over $MgSO_4$. After the filtration and removal of solvent, the residue was purified by silica-gel column chromatography using chloroform/hexane (v/v = 2/1) as eluent, and washed by dichloromethane to give **1L** with m.p. 136.7 – 137.0 °C. Yield: 1.62 g, 37.4%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 17.07 (s, 1H), 8.68 (s, 3H), 8.03 (d, 6H, 8.45 Hz), 7.00 (d, 6H, 8.45Hz), 6.95 (s, 3H), 4.06 (t, 6H), 1.84 (quintet, 6H), 1.2-1.54 (m, 54H), 0.89 (t, 9H). MS (MALDI-TOF, *m/z*) cal: 1068.7, found: 1069.2 $[M]^+$. Elemental Analysis: CHN cal: 77.49% C, 9.05% H. Found: 77.48% C, 9.07% H. IR (ATR / cm^{-1}) 2920, 2851, 1603, 1581, 1468, 1248, 1177, 789.

BF_2dk complex 1. Ligand **1L** (0.2 g, 0.187 mmol) was dissolved in toluene/AcOH (v/v = 1/1, 11 ml) and was heated to 100 ºC. BF_3•Et_2O (0.087 g, 0.617 mmol) was added in less excess and boiled for several minutes. The solution was cooled to room temperature and was isolated by filtration, washed by the reaction solvent several times to give **1** with d.p. 200 °C. Yield: 0.21 g, 92.6%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.01 (s, 3H), 8.32 (d, 6H, 8.97 Hz), 7.33 (s, 3H), 7.10 (d, 6H, 8.97 Hz), 4.14 (t, 6H), 1.86 (quintet, 6H), 1.25-1.58 (m, 54H), 0.89 (t, 9H). MS (MALDI-TOF, *m/z*) cal: 1212.7, found: 1192.9 $[M-F]^+$. Elemental

Analysis: CHN cal: 68.33% C, 7.73% H. Found: 68.13% C, 7.76% H. IR (ATR / cm^{-1}) 2922, 2853, 1601, 1572, 1530, 1495, 1267, 1175, 1040, 797.

Ligand 2L. 60% NaH (6.08 g, 152 mmol) was added to round flask and atmosphere was substituted to nitrogen. Anhydrous DME (100 ml) solution containing methyl-*p*-dodecanoxy benzoate (9.0 g, 28.1 mmol) and *para*-dodecanoxyacetophenone (9.4 g, 30.9 mmol) were poured into the flask in ice bath. The solution was stirred at 80 ºC for 7.5 hrs. After the reactant was cooled to room temperature, it was poured into ice water (600 ml). 2.5 N HCl aq. was added to neutralize excess NaH. The mixture was extracted with chloroform, and the organic phase was dried over $MgSO_4$. After the filtration and removal of solvent, the residue was washed by acetone to afford **2L** with m.p. 92 – 93 °C. Yield: 13.3 g, 80%. ^{1}H-NMR (300 MHz, $CDCl_3$): *δ* 17.13 (s, 1H), 7.94 (d, 4H, 8.93 Hz), 6.96 (d, 4H, 8.93 Hz), 6.73 (s, 1H), 4.03 (t, 4H), 1.81 (quintet, 4H), 1.2-1.56 (m, 36H), 0.88 (t, 6H). MS (MALDI-TOF, *m/z*) cal: 592.4, found: 592.7 $[M]^+$. Elemental Analysis: CHN cal: 79.01% C, 10.20% H. Found: 78.93% C, 10.29% H. IR (ATR / cm^{-1}) 2918, 2849, 1605, 1585, 1501, 1464, 1252, 1175, 783.

BF_2dk complex 2. Ligand **2L** (0.2 g, 0.337 mmol) was dissolved in toluene (5 ml) and was heated to 100 ºC. BF_3•Et_2O (0.053 g, 0.371 mmol) was added in less excess and boiled for several minutes. The solution was cooled to room temperature and was isolated by filtration, washed by toluene to give **2** with m.p. 139.5-140.8 °C. Yield: 0.19 g, 88%. ^{1}H-NMR (300 MHz, $CDCl_3$): *δ* 8.11 (d, 4H, 8.97 Hz), 7.01 (s, 1H), 7.00 (d, 4H, 8.97 Hz), 4.07 (t, 4H), 1.83 (quintet, 4H), 1.2-1.54 (m, 36H), 0.88 (t, 3H). MS (MALDI-TOF, *m/z*) cal: 640.4, found: 620.7 $[M-F]^+$. Elemental Analysis: CHN cal: 73.11% C, 9.28% H. Found: 73.12% C, 9.33% H. IR (ATR / cm^{-1}) 2918, 2849, 1607, 1545, 1501, 1468, 1246, 1182, 1032, 804.

Ligand 3L. 60% NaH (3.38 g, 84.5 mmol) was added to round flask and atmosphere was substituted to nitrogen. Anhydrous DME (55 ml) solution containing dimethyl isophthalate (1.52 g, 7.82 mmol) and *para*-dodecanoxyacetophenone (5.0 g, 16.4 mmol) were poured into the flask in ice bath. The solution was stirred at 80 ºC for 10.5 hrs. After the reactant was cooled to room temperature, it was poured into ice water (300 ml). 2.5 N HCl aq. was added to neutralize excess NaH. The mixture was extracted with chloroform, and the organic phase was dried over $MgSO_4$. After the filtration and removal of solvent, the residue was washed with acetone and then purified by silica-gel column chromatography using chloroform as eluent to give **3L** with m.p. 126.7 – 127.0 °C. Yield: 1.91 g, 33.1%. ^{1}H-NMR (300 MHz, $CDCl_3$): *δ* 17.02 (s, 2H), 8.54 (s, 1H), 8.13 (d, 2H, 7.73 Hz), 8.01 (d, 4H, 8.56 Hz), 7.61 (t, 1H, 7.73 Hz), 6.99 (d, 4H, 8.56 Hz), 6.87 (s, 2H), 4.05 (t, 4H), 1.82 (quintet, 4H), 1.2-1.54 (m, 36H), 0.88 (t, 6H). MS (MALDI-TOF, *m/z*) cal: 738.5, found: 738.7 $[M]^+$. Elemental Analysis: CHN cal: 78.01% C, 9.00% H. Found: 78.03% C, 8.99% H. IR (ATR / cm^{-1}) 2918, 2849, 1605, 1585, 1464, 1254, 1177, 779. UV ($CHCl_3$):

BF_2dk complex 3. Ligand **3L** (0.2 g, 0.271 mmol) was dissolved in toluene/AcOH (v/v = 1/1, 11 ml) and was heated to 100 ºC. BF_3•Et_2O (0.085 g, 0.596 mmol) was added in less excess and boiled for several

minutes. The solution was cooled to room temperature and was isolated by filtration, washed by the reaction solvent and hexane several times to give **3** with d.p. 200 °C. Yield: 0.18 g, 80%. ^{1}H-NMR (300 MHz, $CDCl_3$, 45ºC): *δ* 8.77 (s, 1H), 8.38 (d, 2H, 8.15 Hz), 8.22 (d, 4H, 8.87 Hz), 7.73 (t, 1H, 8.15 Hz), 7.18 (s, 2H), 7.06 (d, 2H, 8.87 Hz), 4.12 (t, 6H), 1.85 (quintet, 4H), 1.16-1.54 (m, 54H), 0.88 (t, 3H). MS (MALDI-TOF, *m/z*) cal: 834.5, found: 814.8 $[M-F]^+$. Elemental Analysis: CHN cal: 69.07% C, 7.73% H. Found: 69.10% C, 7.70% H. IR (ATR / cm^{-1}) 2920, 2851, 1607, 1549, 1499, 1252, 1182, 1042, 808.

Ligand 4L. 60% NaH (2.52 g, 63 mmol) was added to round flask and atmosphere was substituted to nitrogen. Anhydrous DME (42 ml) solution containing dimethyl terephthalate (1.33 g, 5.97 mmol) and *para*-dodecanoxyacetophenone (4.0 g, 13.1 mmol) were poured into the flask in ice bath. The solution was stirred at 80 ºC for 10.5 hrs. After the reactant was cooled to room temperature, it was poured into ice water (200 ml). 2.5 N HCl aq. was added to neutralize excess NaH. The mixture was extracted with chloroform, and the organic phase was dried over $MgSO_4$. After the filtration and removal of solvent, the residue was washed with acetone and with dichloromethane to give 4**L** with m.p. 151.4 – 152 °C. Yield: 1.08 g, 24.5%. ^{1}H-NMR (300 MHz, $CDCl_3$): *δ* 16.9 (s, 2H), 8.06 (s, 4H), 7.99 (d, 4H, 8.76 Hz), 6.98 (d, 4H, 8.76 Hz), 6.85 (s, 2H), 4.05 (t, 4H), 1.82 (quintet, 4H), 1.2-1.58 (m, 36H), 0.89 (t, 6H). MS (MALDI-TOF, *m/z*) cal: 738.5, found: 739.1 $[M]^+$. Elemental Analysis: CHN cal: 78.01% C, 9.00% H. Found: 77.73% C, 8.91% H. IR (ATR / cm^{-1}) 2918, 2849, 1605, 1506, 1471, 1254, 1179, 775.

BF_2dk complex 4. Ligand **4L** (0.2 g, 0.271 mmol) was dissolved in toluene/AcOH (v/v = 1/1, 11 ml) and was heated to 100 ºC. BF_3•Et_2O (0.085 g, 0.596 mmol) was added in less excess and boiled for several minutes. The solution was cooled to room temperature and was isolated by filtration, washed by reaction solvent and hexane several times to give **4** with d.p. 200 °C. Yield: 0.19 g, 85.0%. ^{1}H-NMR (300 MHz, $CDCl_3$, 45ºC): *δ* 8.25 (s, 4H), 8.20 (d, 4H, 9.02 Hz), 7.15 (s, 2H), 7.05 (d, 4H, 9.02 Hz), 4.12 (t, 4H), 1.84 (quintet, 4H), 1.25-1.60 (m, 36H), 0.88 (t, 6H). MS (MALDI-TOF, *m/z*) cal: 834.5, found: 815.2 $[M-F]^+$. Elemental Analysis: CHN cal: 69.07% C, 7.73% H. Found: 68.84% C, 7.72% H. IR (ATR / cm^{-1}) 2920, 2855, 1601, 1537, 1487, 1473, 1271, 1042, 800.

2. Supplementary Characterizations

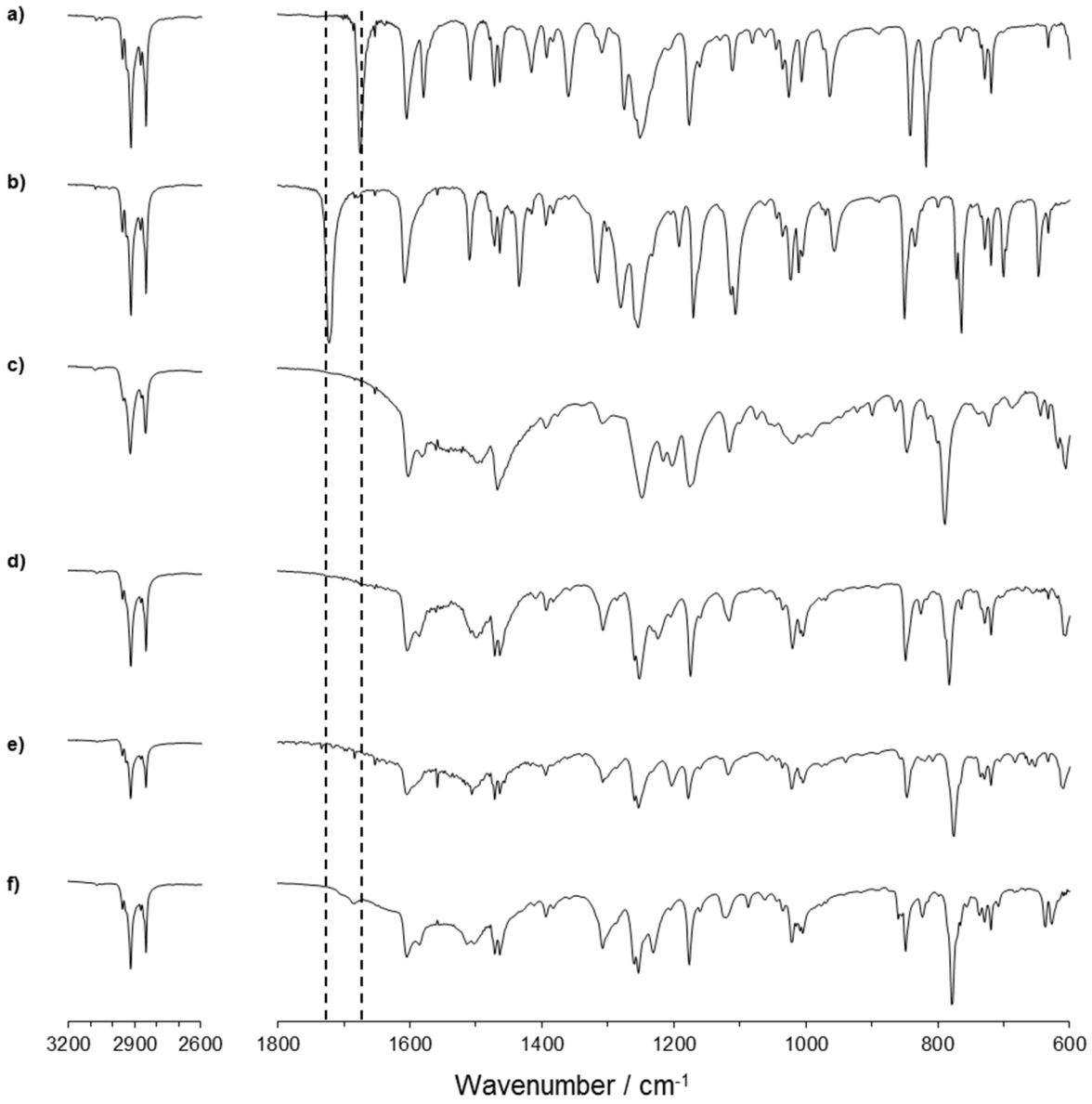


Fig. S1 FT-IR spectra of (a) **C_{12}ketone**, (b) **C_{12}methylester** (for abbreviation, see Scheme S1) and ligands (c) **1L**, (d) **2L**, (c) **3L** and (f) **4L**.

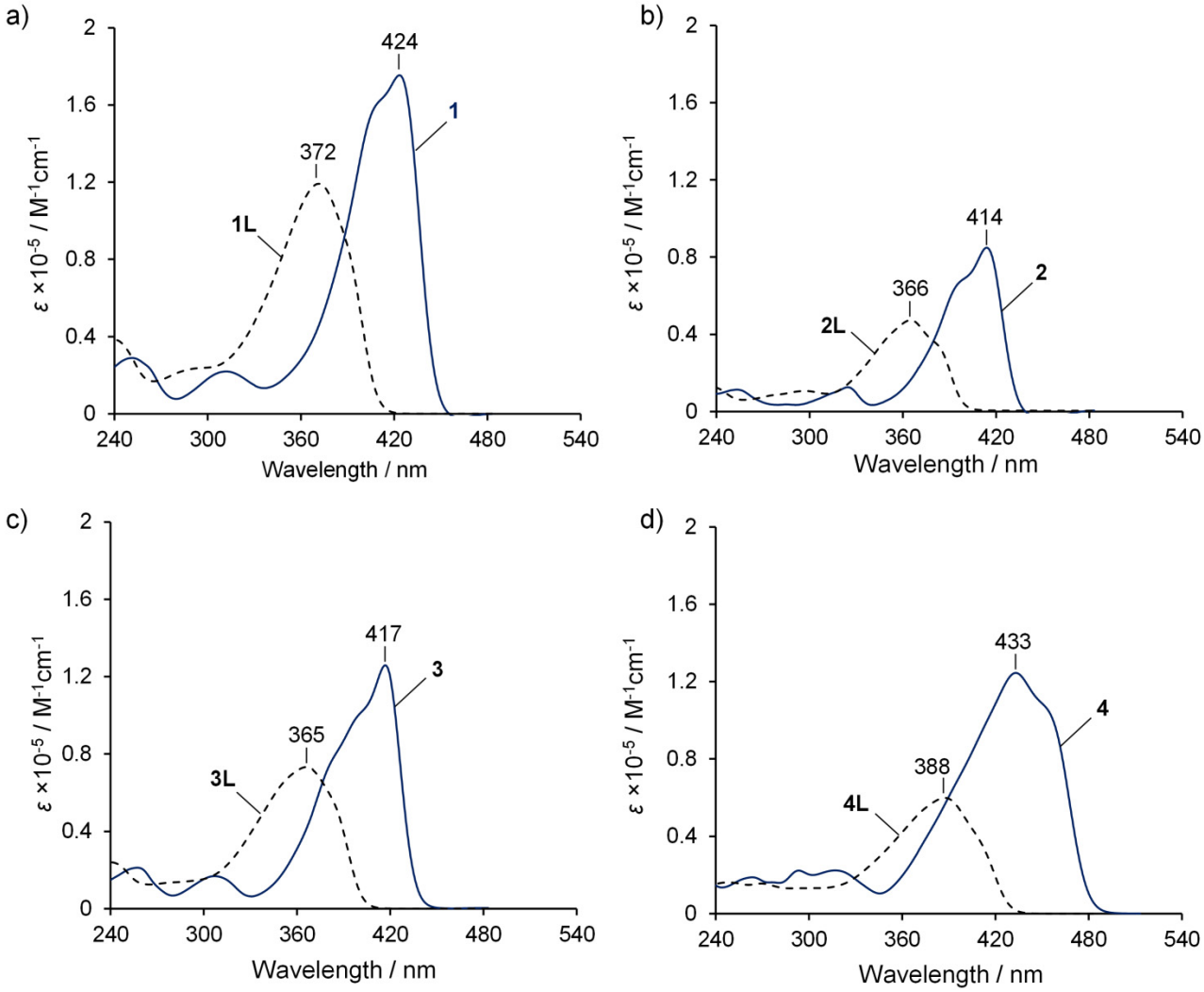


Fig. S2 UV-vis absorption spectra of BF_2dk complexes (**1**–**4**) and the corresponding ligands (**1L**–**4L**) in chloroform at 10 μM, 20 ºC. (a) **1** and **1L**, (b) **2** and **2L**, (c) **3** and **3L**, and (d) **4** and **4L**.

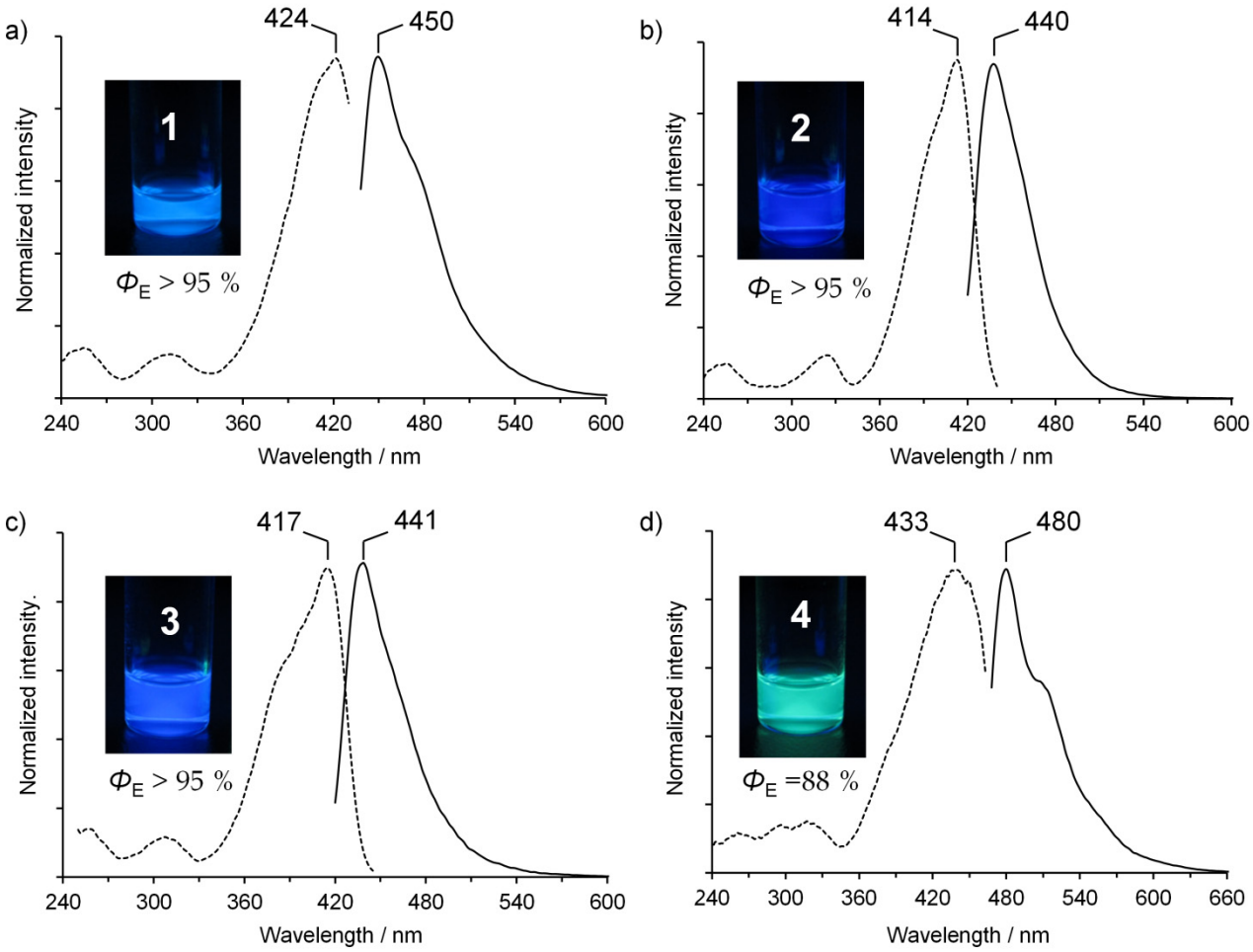


Fig. S3 Emission (solid line) and excitation (dashed line) spectra of a series of BF_2dk complexes **1**–**4** in chloroform at 10 μM, 20 °C. Insets show the photographs of the solutions illuminated by a UV lamp at 365 nm. Φ_E: absolute photoluminescence quantum yield.

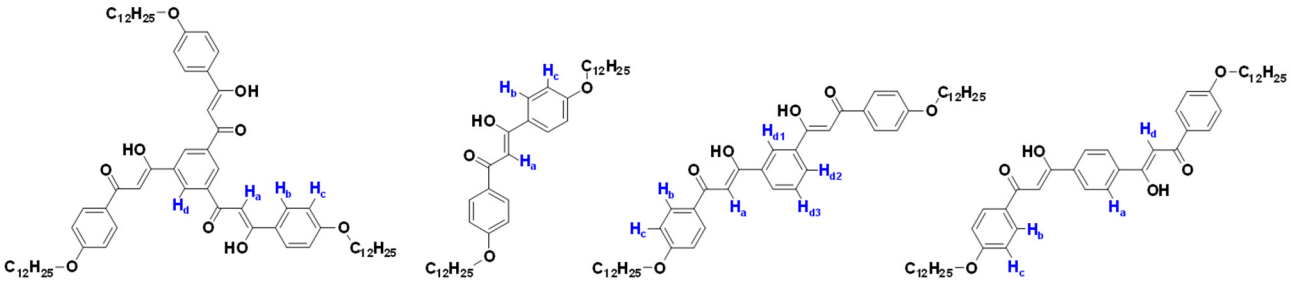
Table S1. Spectroscopic Properties of Complexes **1**-**4** and Ligands **1L**-**4L** in Chloroform at 20 °C (10 μM).

Complex	λ_{max}	ε_{max}	λ_{em}	Φ_E
1	424	175,400	450	> 95
2	414	84,500	440	> 95
3	417	125,800	441	> 95
4	433	124,200	480	88

Ligand	λ_{max}	ε_{max}
1L	372	119,200
2L	366	47,230
3L	365	73,300
4L	388	59,840

λ_{max}: absorption maximum in nm, ε_{max}: molar absorption coefficient in $M^{-1}cm^{-1}$, λ_{em}: peak emission wavelength in nm, Φ_E: absolute photoluminescence quantum yield in %.

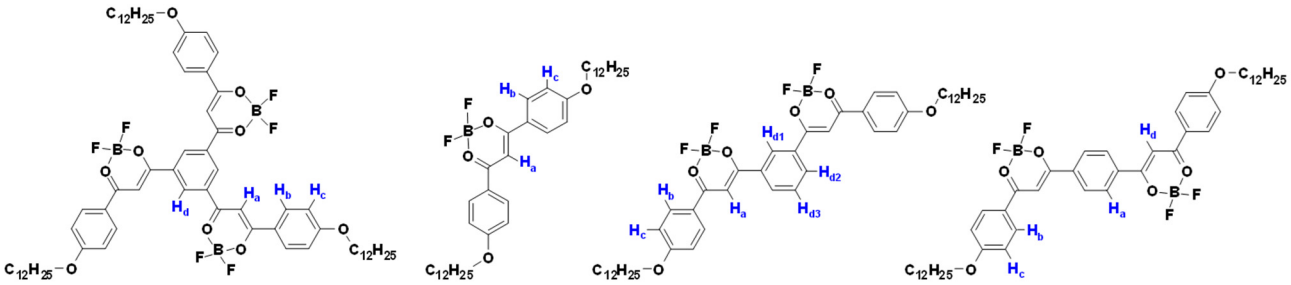
Table S2. Chemical Shifts of Enolic and Aromatic Protons for the Ligands **1L**–**4L** in Chloroform at 10 μM, 20 °C.



1L **2L** **3L** **4L**

Ligand	Enolic proton	H_a	H_b	H_c	H_d
1L	17.07	6.95	8.03	7.00	8.68
2L	17.17	6.73	7.94	6.96	–
3L	17.02	6.86	8.01	6.99	8.54, 8.13, 7.61
4L	16.94	6.85	7.99	6.98	8.06

Table S3. Chemical Shifts of Fluorines and Aromatic Protons for the Complexes **1**–**4** in Chloroform at 10 μM, 20 °C.



1 **2** **3** **4**

Complex	F-signal	H_a	H_b	H_c	H_d
1	-139	7.33	8.32	7.10	9.01
2	-140.8	7.01	8.11	7.00	–
3	-139.4	7.18	8.22	7.06	8.77, 8.38, 7.73
4	-139.5	7.15	8.20	7.05	8.25

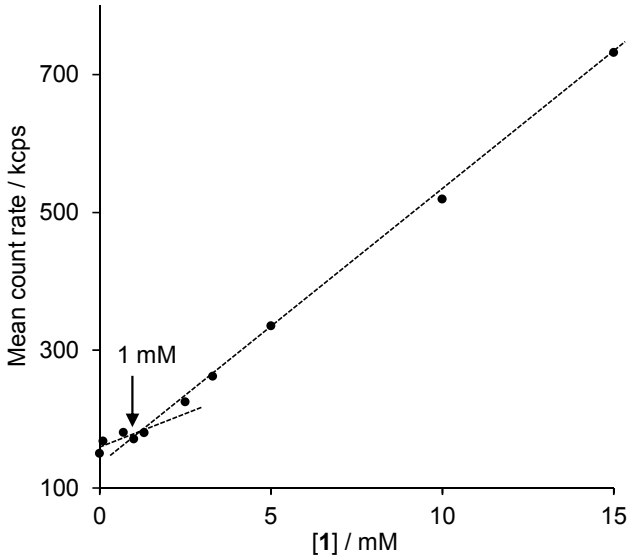


Fig. S4 A plot of mean count rate as a function of the concentration of **1** in chloroform at 20 °C.

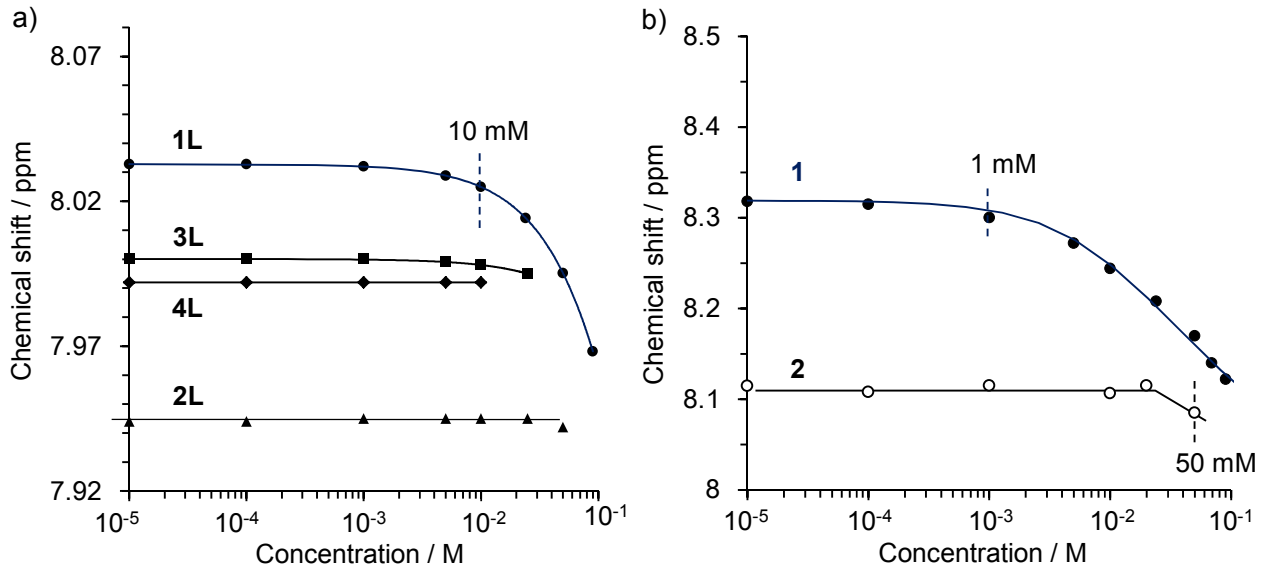


Fig. S5 Changes in the chemical shift of H_b protons for (a) ligands (**1L**–**4L**) and (b) BF_2dk complexes (**1**, **2**) as a function of their concentrations.

Table S4. Pseudo Association Constants (K_2) Determined by Using ^{1}H- and ^{19}F-NMR Spectroscopies.

	Temperature	Complex 1			Ligand 1L		
		Fluorine	H_d	Average / M^{-1}	H_a	H_c	Average / M^{-1}
K_2	20 °C	33.2	20.8	27.0±6.2	0.94	0.64	0.79±0.15
(M^{-1})	30 °C	29.3	20.6	25.0±4.3	–	–	–

VPO analysis

In order to examine the aggregation properties of the complex **1** in chloroform, VPO measurements were carried out. The obtained data were analyzed by using dimer or infinite (isodesmic) association models described by Martin[S1]. We have assumed that $CHCl_3$ solution of **1** behaves like an ideal solution and the activity coefficient of monomeric species and aggregates are unities. The osmotic coefficient for the dimer model (Φ'_D) was obtained as follows;

$$\Phi'_D = \left(4L - 1 + \sqrt{8L + 1}\right)/8L \qquad \text{(eq. S1)}$$

where $L = K_2 C$ and C is the molar concentration.

In addition, the osmotic coefficient for the isodesmic model (Φ'_{iso}) was calculated by using following equation;

$$\Phi'_{iso} = \left(-1 + \sqrt{4L + 1}\right)/2L \qquad \text{(eq. S2)}$$

where $L = K_{iso} C$. The Φ' versus concentration data were analyzed by nonlinear least squares fitting using Microsoft Excel 2010 Solver Add-In. Each number average molecular weight (M_n) at varied concentrations is given by $M_n = M_1\ (1212.89)/\Phi'$, where M_1 is the molecular weight of monomeric species.

Fig. S5 shows the plot of M_n for the complex **1** in chloroform as a function of the concentration. The red and black curves indicate the calculated profiles according to the dimer (eq. S1) and isodesmic (eq. S2) models, respectively. The dimer model is assumed equilibrium between monomers and dimers, while the isodesmic model is assumed the formation of higher aggregates, in which all association constants for individual steps are equal. As shown in Fig. S6, the best fitting curve was obtained by using eq. S1 with K_2 value of 45.2 M^{-1}, indicating the formation of dimeric aggregates which are in equilibrium with the monomeric species.

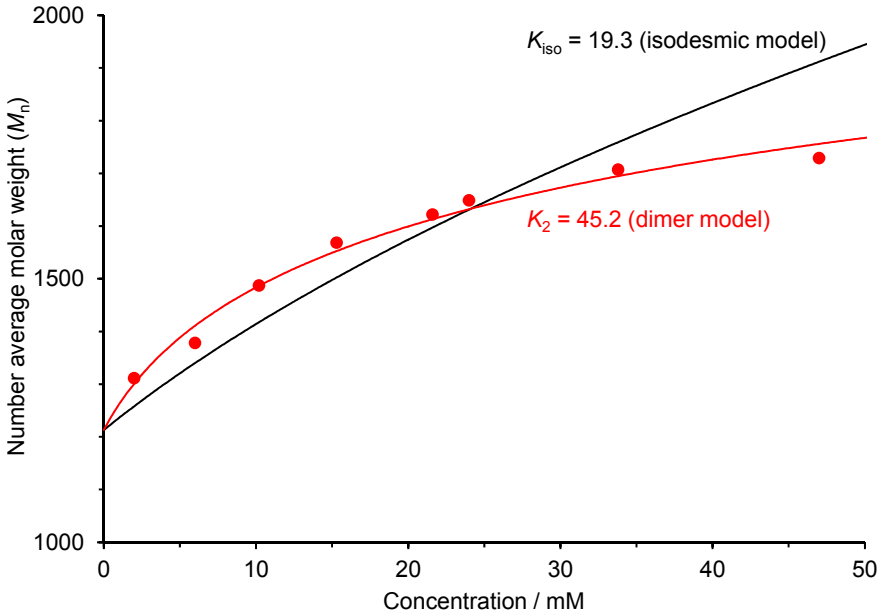


Fig. S6 Concentration dependency of number average molecular weight (M_n) of the complex **1** determined by VPO measurements in chloroform at 30 °C. Filled circles: experimental data, Red line: calculated curve by using eq. S1 (dimer model) with K_2 = 45.2 M^{-1}, Black line: calculated curve by using eq. S2 (isodesmic model) with K_{iso} = 19.3 M^{-1}.

Quantum chemical calculation

Method. The calculations were carried out with B3LYP method and 6-311G(d) basis set using Gaussian 09 program[S2]. Default convergence criteria were used for the SCF calculations and the geometry optimizations. The stability of the geometries was checked with frequency calculations, as well as re-optimizing the geometry after random distortions along selected distortion angles. In case of monomer molecule the optimal geometry is slightly distorted from an ideal planar (ideal symmetry: C_{3v}) one. However, there is no significant difference in optical properties, charge distribution or energy compared to the planar structure (< 0.5 kcal/mol). For simplicity, the parameters of the ideal planar structure are discussed.

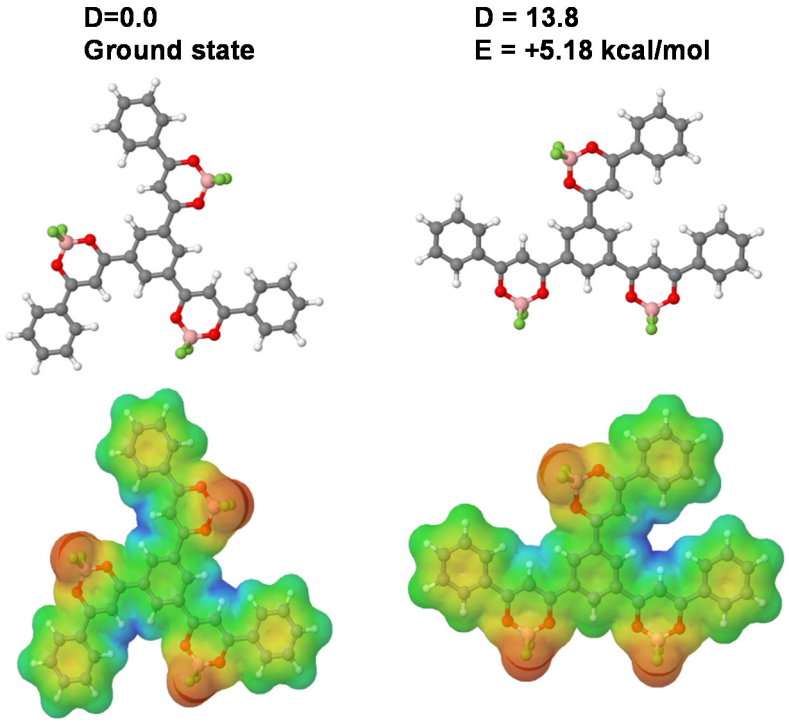


Fig. S7 Geometry of model compound of **1** in two possible conformations.

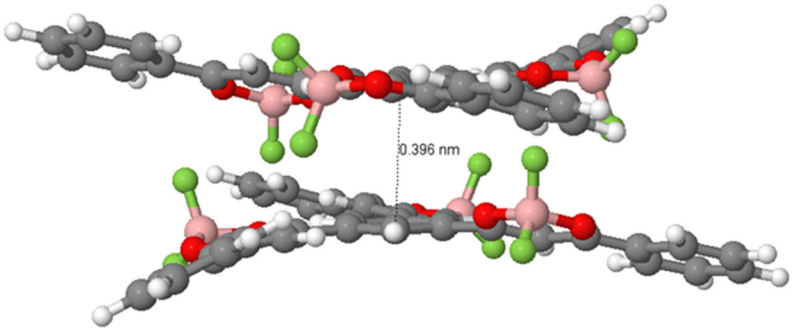


Fig. S8 Geometry of the interlocked dimer formed between two core units.

Table S5. Geometry of the Dimer: Distances Relevant to BF•••H Interactions

Geometry	Distance (Å)			
	F(1)	F(2)	F(3)	Avg.
F-H_a	2.382	2.720	2.350	2.484
F-H_b	2.260	2.204	2.279	2.248
F-H_d	2.833	3.388	2.712	2.978

Table S6. Geometry of the Dimer: Angles Relevant to BF•••H Interactions

Geometry	Angle (deg.)			
	F(1)	F(2)	F(3)	Avg.
B-F..H_a	121.3	121.5	118.4	120.4
B-F..H_b	118.9	123.2	112.0	118.0
B-F..H_d	124.9	125.3	127.3	125.8

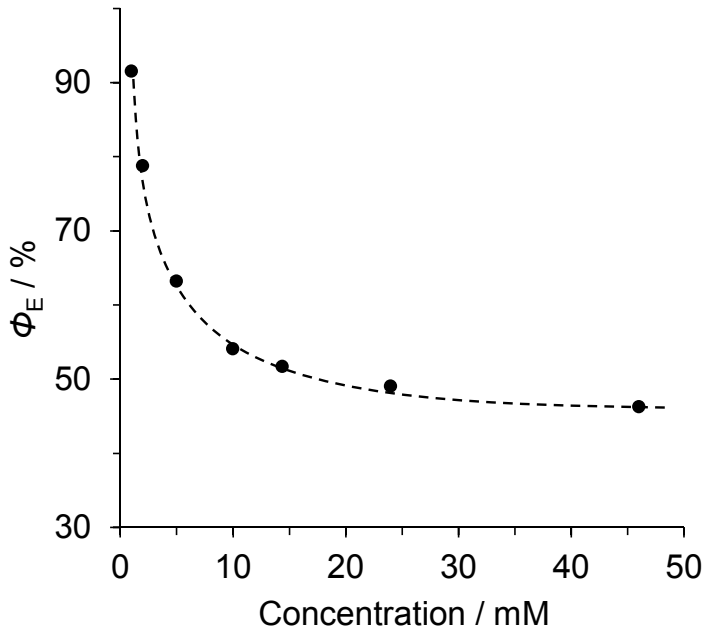


Fig. S9 Photoluminescence quantum yield of the complex **1** as a function of the concentration in $CHCl_3$ at 20 °C.

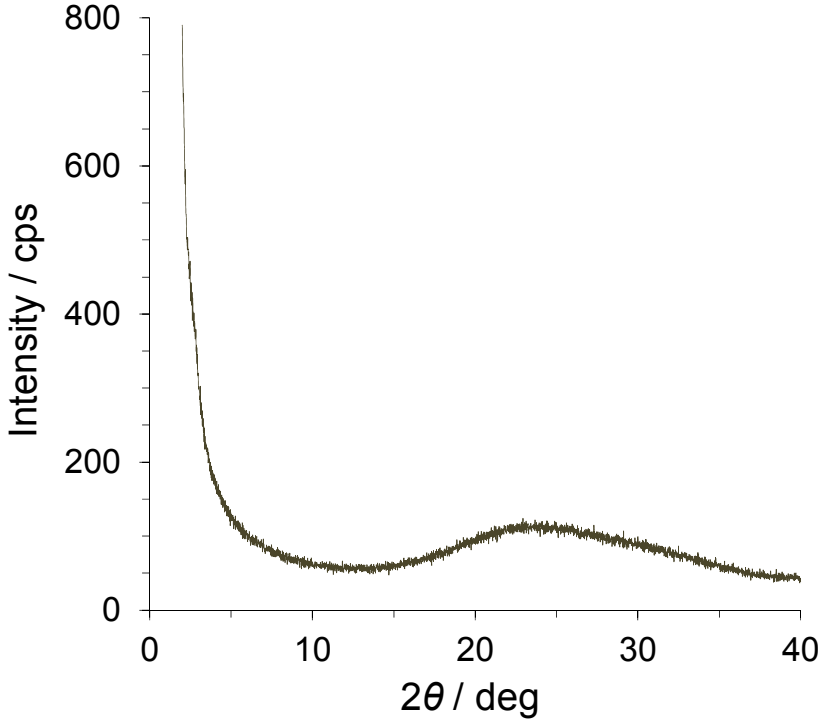


Fig. S10 X-ray diffraction pattern of the drop cast film of the complex **1** prepared from a $CHCl_3$ solution (1.0 mM) on a quartz plate. Cu Kα, λ = 1.5406 Å

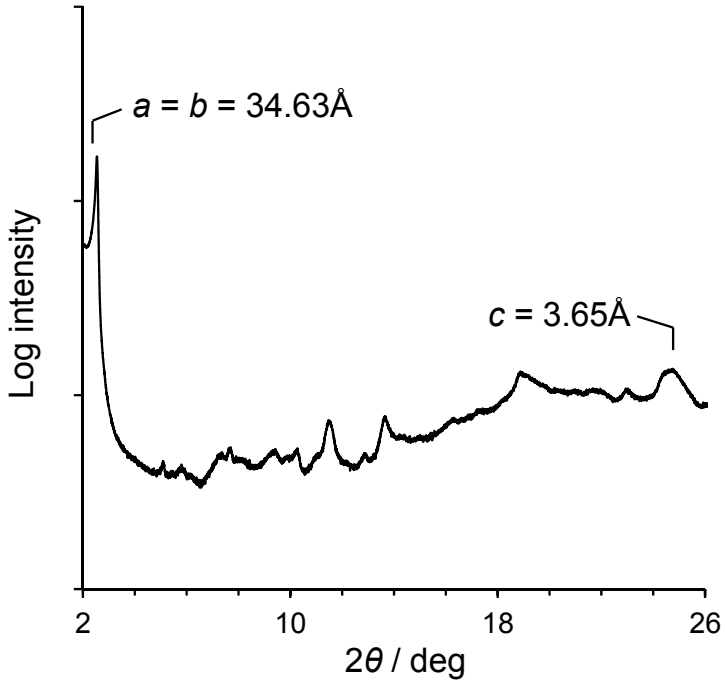


Fig. S11 X-ray diffraction pattern of the complex **1** powder precipitated by evaporating a $CHCl_3$ solution (1.0 mM, 1little). Cu Kα, λ = 1.5406 Å

Table S7. XRD profiles data for complex **1** in the powder state

h k l	exp. / 2ϑ	exp. / deg	cal. / 2ϑ	cal. / deg
1 0 0	2.54	34.70	2.54	34.70
2 0 0	5.10	17.31	5.09	17.35
2 1 0	5.83	15.15	5.69	15.52
2 2 0	7.31	12.09	7.20	12.27
3 0 0	7.70	11.48	7.64	11.57
3 1 0	8.03	11.01	8.05	10.97
3 2 0	9.27	9.53	9.18	9.62
4 0 0	10.27	8.61	10.19	8.68
4 2 0	11.46	7.72	11.39	7.76
4 3 0	12.89	6.87	12.74	6.94
0 0 1 (or 0 0 2)	24.36	3.65	24.37	3.65

The observed XRD data shows diffraction peaks with the ratio of 1 : 1/2 : 1/√5, 1/√8 : 1/3, which is ascribable to the tetragonal columnar crystalline (*Col*$_{tet}$) phase with $a = b$ = 34.7 Å (Fig. S11 and Table S7, ESI). c lattice constant was inferred as 3.65 Å or 7.3 Å depending on whether the crystalline is consisted of the monomeric or the dimeric constituents. Because 3.65 Å is the typical distance for π-π stacking, the elongation process from dimeric species via weak π-π interactions is expected. However the observed low crystallinity indicates that the elongation process from dimeric species is suppressed, which is in agreement with the anti-cooperative characteristics observed for the interlocked dimer (**1**)$_2$.

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