Supplementary Material (ESI) for Chemical Communications

Electronic supplementary information

Remarkable rate acceleration of [4+2] cyclodimerization of an ethynylanthracene derivative on the product crystal surfaces

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Experimental Section (S1)

General: ^{1}H NMR spectra were measured with JEOL AL-300N FT NMR SYSTEM (300 MHz). Thin layer chromatography (TLC) was performed on aluminum plates coated with aluminum oxide gel 60 F254 (Merck). Column chromatography was performed using aluminum oxide 90 standard (MERCK). Chemicals were purchased from Wako Pure Chemical Industries Ltd. and used as received without further purification. X-ray diffraction profile was collected and analyzed with an X-ray diffractometer (Rigaku R-AXIS RAPID/s) with the Mo Kα radiation. Computation of molecular graphics was performed with ORTEP-3 for Windows (Fig. 2a, 2b, and Fig. S6).

Preparation of 2-(anthracene-9-ylethynyl)-1-methylbenzimidazole (BzIm-An): A 200 ml four necked flask was charged with 2-iodo-1-methylbenzimidazole (390 mg, 1.5 mmol), (anthracene-9-ylethynyl)trimethylsilane (430 mg, 1.6 mmol), CuI (15 mg, 0.080 mmol), PPh_3 (8 mg, 0.031 mmol), and tetra-*n*-butylammonium fluoride (in THF 1 mol/L, 4.2 mL) in THF/ triethylamine (40 ml/40 ml). After the solution was degassed by bubbling with N_2 gas for 30 min, $Pd(PPh_3)_2Cl_2$ (57 mg, 0.081 mmol) was added to the reaction flask. Then, the reaction mixture was stirred at 90 °C under Ar atmosphere for 9 hours. The crude product was filtrated and purified by column chromatography over aluminum gel using chloroform to yield 460 mg (91%) of yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.70 (d, J = 8.4 Hz, 2H), 8.55 (s, 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 7.5 Hz, 1H), 7.66 (t, J = 7.2 Hz, 2H), 7.56 (t, J = 7.2 Hz, 2H), 7.42-7.37 (m, 3H), 3.27 (s, 3H). HRMS (ESI): m/z calcd. for $C_{24}H_{17}N_2$ ($[M+H]^+$), 333.13917; found 333.13907.

Preparation of 2-(anthracene-9-ylethynyl)-1-methylimidazole (Im-An): A 200 ml four necked flask was charged with 2-iodo-1-methylimidazole (210 mg, 1.0 mmol), (anthracene-9-ylethynyl)trimethylsilane (280 mg, 1.0 mmol), CuI (10 mg, 0.053 mmol), PPh_3 (6 mg, 0.023 mmol), and tetra-*n*-butylammonium fluoride (in THF 1 mol/L, 2.8 mL) in THF/triethylamine (20 ml/20 ml). After the solution was degassed by bubbling with N_2 gas for 30 min, $Pd(PPh_3)_2Cl_2$ (38 mg, 0.053 mmol) was added to the reaction flask. Then, the reaction mixture was stirred at 90 °C under Ar atmosphere for 11 hours. The crude product was filtrated and purified by column chromatography over aluminum gel using chloroform to yield 170 mg (60%) of yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.64 (d, J = 8.1 Hz, 2H), 8.49 (s, 1H), 8.04 (d, J = 8.1 Hz, 2H), 7.61 (t, J = 8.1 Hz, 2H), 7.53 (t, J = 8.1 Hz, 2H), 7.21 (d, J = 1.2 Hz, 1H), 7.06 (t, J = 1.2 Hz, 1H), 4.00 (s, 3H). HRMS (ESI): m/z calcd. for $C_{20}H_{15}N_2$ ($[M+H]^+$), 283.12352; found 283.12345.

Reaction procedures and analysis: The isolated $(BzIm\text{-}An)_2$ (2.5×10^{-3} mol dm^{-3}) was dissolved in $CDCl_3$/*n*-hexane-d_{14} (3:1, v/v), and the solution was kept at room temperature (298

K) for 12 days. The reaction solution was then analyzed by ^{1}H NMR spectroscopy, in which no retro-Diels-Alder product (BzIm-An) was observed. The thermal cyclodimerization reaction of BzIm-An was carried out in the presence of Lewis acid (zinc triflate). The monomer BzIm-An (5.0×10^{-5} mol dm^{-3}) was added to an NMR tube that contained an [$^2H_3$]acetonitrile (CD_3CN) solution (0.6 mL) of zinc triflate (1.5×10^{-4} mol dm^{-3}) under an atmospheric pressure of argon. The solution was kept at 313 K for 14 days. The reaction solution was analyzed by ^{1}H NMR spectroscopy, and no cyclodimer formation was confirmed. The cyclodimerization reaction of BzIm-An was also examined at high temperature as follows. The monomer BzIm-An (1.7×10^{-3} mol dm^{-3}) was dissolved in CD_3CN, and the solution was kept at 333K for 21 days. The conversion yield of BzIm-An to $(BzIm\text{-}An)_2$ was determined to be 3% by comparison of the integration of ^{1}H NMR signal due to $(BzIm\text{-}An)_2$ and BzIm-An.

Spectral measurements: UV-visible absorption and fluorescence spectra were measured with HITACHI F-4500Fluorescence spectrometer and Jasco V-660 spectrophotometer, respectively. Emission quantum yields of BzIm-An and $(BzIm\text{-}An)_2$ were measured in the solid state, by utilizing a calibrated integrating sphere. All measurements were performed at room temperature (298 K).

Crystallization: $(BzIm\text{-}An)_2$ was crystallized by slow evaporation from a chloroform/*n*-hexane (1:1, v/v) solution of BzIm-An (6.9×10^{-3} mol dm^{-3}). Blue and yellow fluorescent crystals appeared after two weeks. These two crystals were separated using metal needles into individual crystals, and the conversion of BzIm-An to $(BzIm\text{-}An)_2$ was determined to be up to 75%. $(BzIm\text{-}An)_2$ was identified by HRMS (ESI), NOE, NOESY, COSY, and ^{1}H NMR spectroscopy (Fig. S2-S5 in the Supporting Information). **$(BzIm\text{-}An)_2$:** ^{1}H NMR (300 MHz, CD_3CN): δ 8.44 (s, 1H, H_a), 7.95 (d, J = 8.7 Hz, 2H, H_b), 7.85 (d, J = 6.6 Hz, 2H, H_c), 7.75 (d, J = 7.5 Hz, 3H, H_d, 27% NOE was detected when irradiated at H_i), 7.51 (d, J = 8.1 Hz, 1H, H_e), 7.27-7.39 (m, 6H, H_f and H_n), 7.16-7.26, [m, 8H, H_g (12% NOE was detected when irradiated at H_k), H_l (3% NOE was detected when irradiated at H_j), and H_m], 6.98-7.11, (m, 3H, H_h, 4% NOE was detected when irradiated at H_j), 5.97 (s, 1H, H_i, 3% NOE was detected when irradiated at H_j), 3.17 (s, 1H, H_j), 2.65 (s, 1H, H_k). HRMS (ESI): m/z calcd for 665.27052; found 665.27078. A yellow single crystal of the BzIm-An was obtained by slow evaporation (within three weeks) of a toluene solution of BzIm-An. A single crystal of the BzIm-An was also grown from slow evaporation of chloroform, *n*-hexane, dichloromethane, and dichloromethane/*n*-hexane (1:1, v/v) solutions of BzIm-An over a couple of weeks, where no $(BzIm\text{-}An)_2$ crystal was formed from those solutions. A yellow single crystal of the Im-An was obtained by slow evaporation of a chloroform/*n*-hexane (1:1, v/v) solution of Im-An (5.9×10^{-3} mol dm^{-3}). Protonated BzIm-An ($BzIm\text{-}AnH^+$) was crystallized by slow evaporation from a

$CHCl_3$ solution of BzIm-An (6.9×10^{-3} mol dm^{-3}) in the presence of a large amount of trifluoroacetic acid (ca. 0.1 mol dm^{-3}). The promoting effect of a catalytic amount of Brønsted acid catalyst on the cyclodimerization reaction was examined as follows. Monomer BzIm-An (1.3×10^{-3} mol dm^{-3}) was dissolved in chloroform/*n*-hexane (1:1, v/v) in the presence of 1 mol% trifluoroacetic acid (1.3×10^{-5} mol dm^{-3}). Slow evaporation of the resulting solution yielded yellow powder after 10 days. The resulting yellow powder was dissolved in CD_3CN to perform ^1H NMR experiments, in which no cycloadduct [$(BzIm\text{-}An)_2$] was observed. All crystallization experiments were carried out at room temperature (298 K) under dark. The crystallization solvent (spectroscopic-grade), chloroform was obtained from Nacalai Tesque. Dichloromethane, *n*-hexane, and toluene were purchased from Wako Pure Chemicals.

Kinetic analysis: Kinetic analysis of crystallization of $(BzIm\text{-}An)_2$ was performed as follows. Monomer BzIm-An (6.9×10^{-3} mol dm^{-3}) was dissolved in chloroform/*n*-hexane (1:1, v/v), and the BzIm-An solution was introduced into sample tubes. Those sample tubes were kept under the same conditions. Under these conditions, the solution reached saturation level at 12 days and initial $(BzIm\text{-}An)_2$ crystals were generated in each sample tube. The yields of $(BzIm\text{-}An)_2$ were determined at 1, 3, 4, 6, 8, 9, 11, 13, 15, and 17 days from those sample tubes by comparison of the integration of ^1H NMR signal of $(BzIm\text{-}An)_2$ and BzIm-An. In order to determine the conversion yield of BzIm-An to $(BzIm\text{-}An)_2$, the crystallization solution in the sample tube was quickly evaporated, and the resulting monomer/dimer mixture was dissolved in CD_3CN to perform ^1H NMR experiments. We have confirmed that rapid evaporation (within 5 min) of monomer/dimer solutions results in no appreciable change of monomer/dimer ratio. Kinetic analysis of crystallization of $(BzIm\text{-}An)_2$ in the presence of the product $(BzIm\text{-}An)_2$ crystals was also examined as follows. Monomer BzIm-An (23.2 mg) was dissolved in 6 mL of chloroform/*n*-hexane (1:1, v/v), and the BzIm-An solution (1 mL) was introduced into sample tubes containing the isolated $(BzIm\text{-}An)_2$ crystals (2.20 mg). Under these conditions, the initially introduced $(BzIm\text{-}An)_2$ crystals were not dissolved in the monomer solution. Those sample tubes were kept under the same conditions. The conversion yield was determined at 1, 2, 4, 5, 6, and 14 days by the same procedure as employed in kinetic analysis of crystallization of $(BzIm\text{-}An)_2$ in the absence of $(BzIm\text{-}An)_2$ crystals (vide supra). In this case, the $(BzIm\text{-}An)_2$ crystals added initially were subtracted from the yield. All crystallization experiments were carried out at room temperature (298 K) under dark.

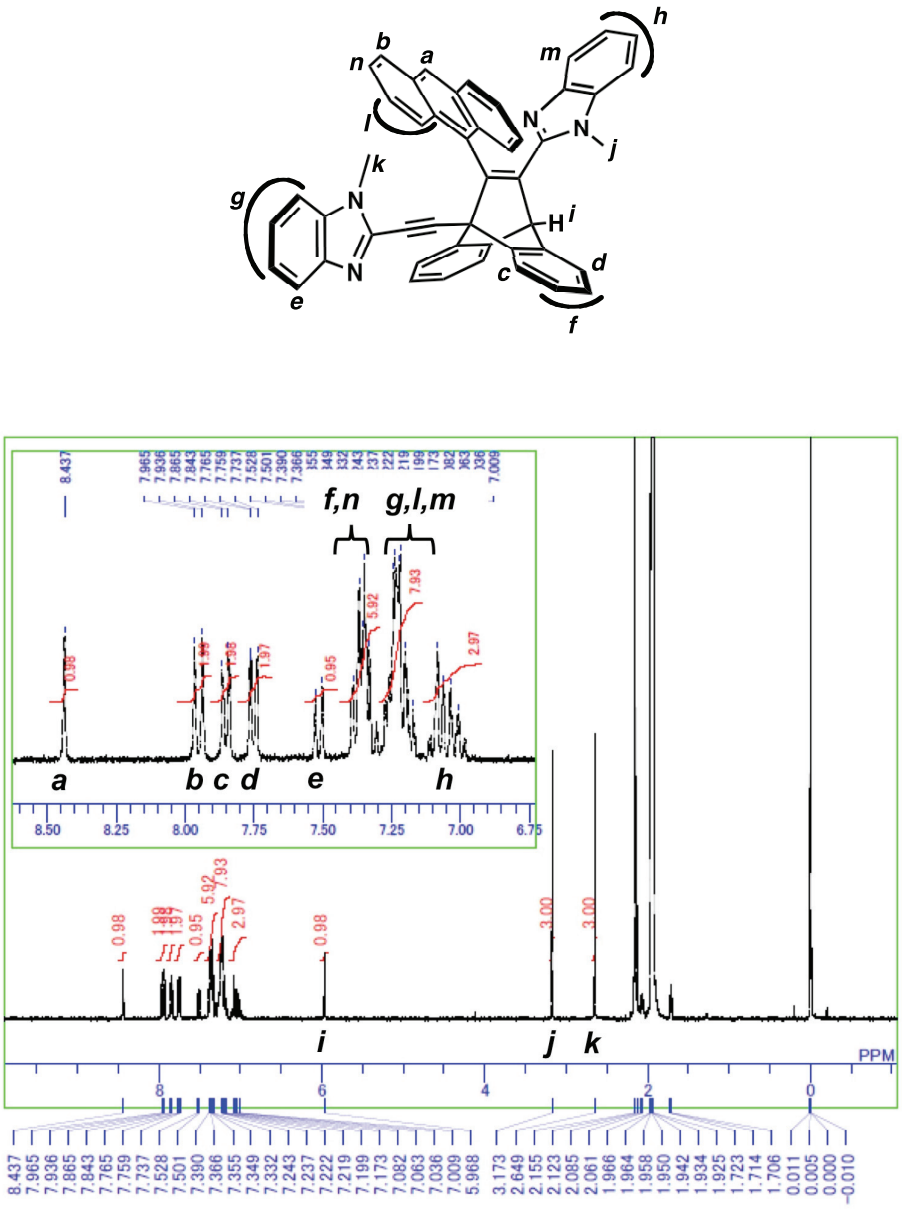
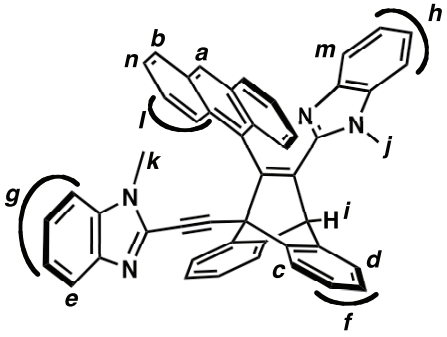


Fig. S2 ^{1}H NMR of (BzIm-An)$_2$ in CD_3CN at 298 K.



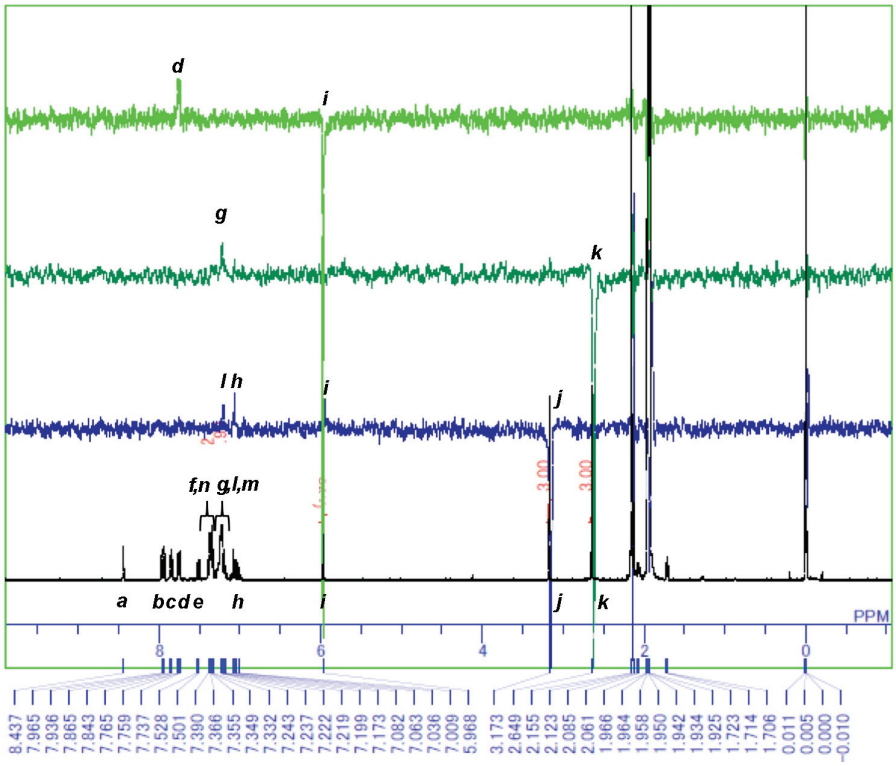


Fig. S3 NOE of $(BzIm\text{-}An)_2$ in CD_3CN at 298 K.

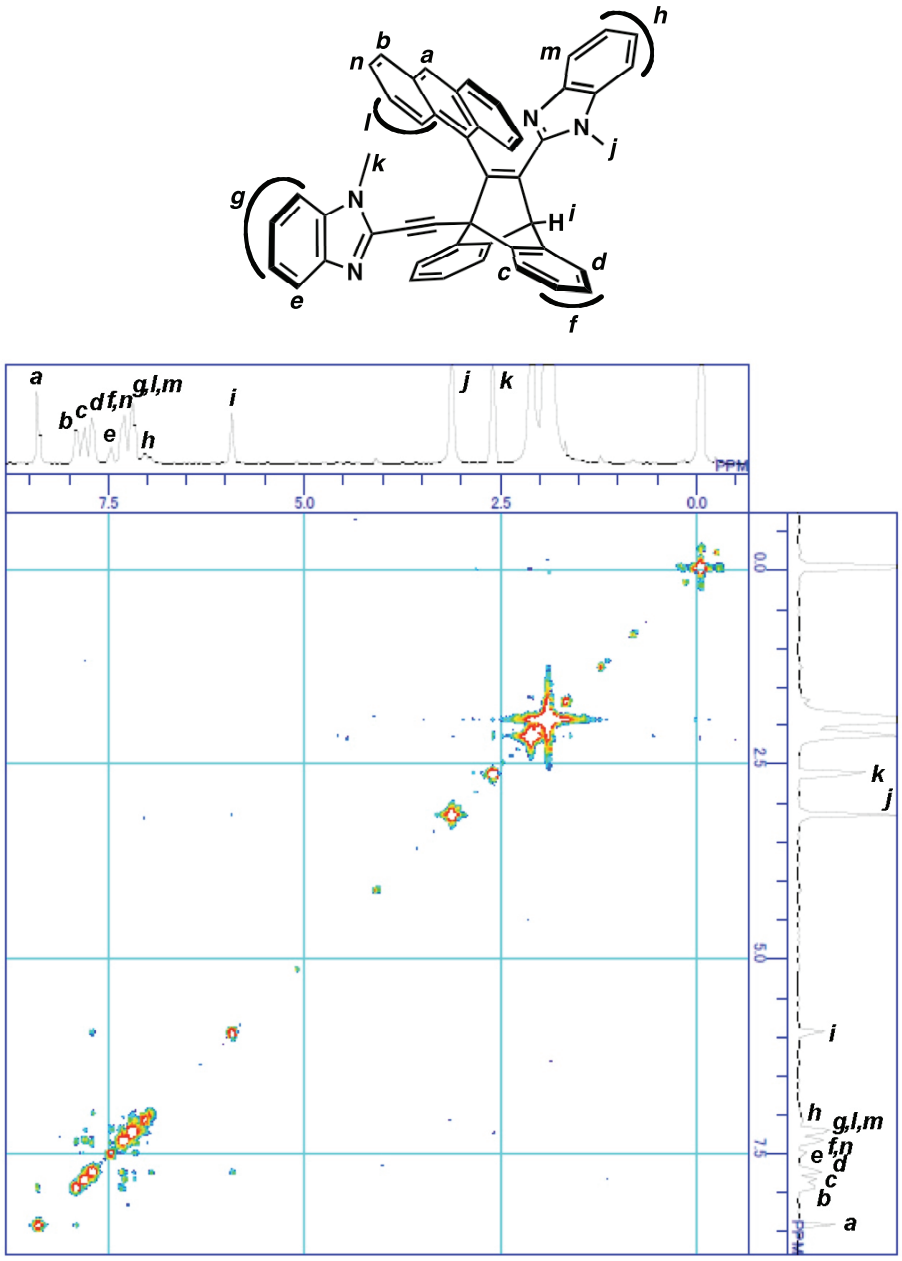


Fig. S4 NOESY of $(BzIm\text{-}An)_2$ in CD_3CN at 298 K.

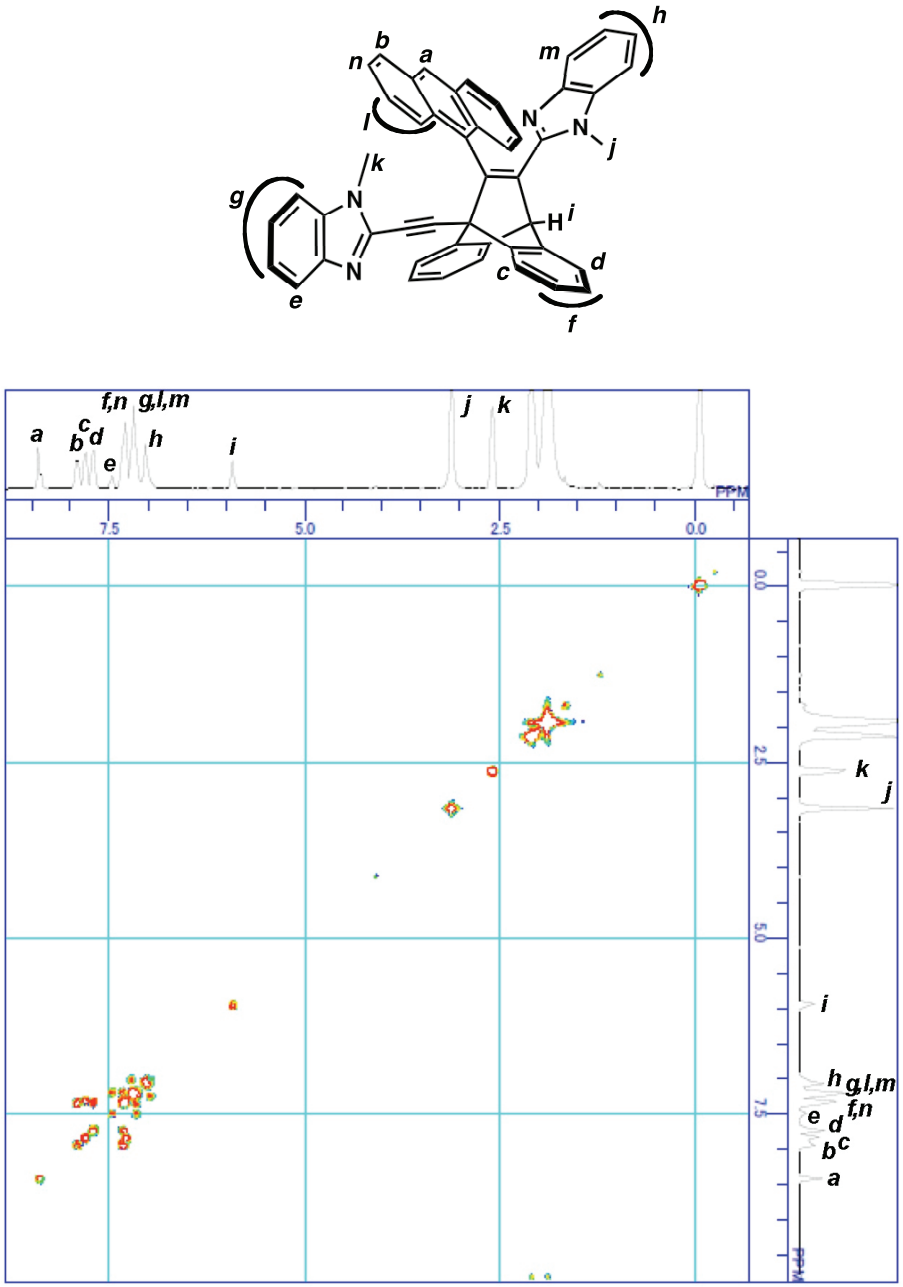


Fig. S5 ^{1}H, ^{1}H COSY of $(BzIm\text{-}An)_2$ in CD_3CN at 298 K.

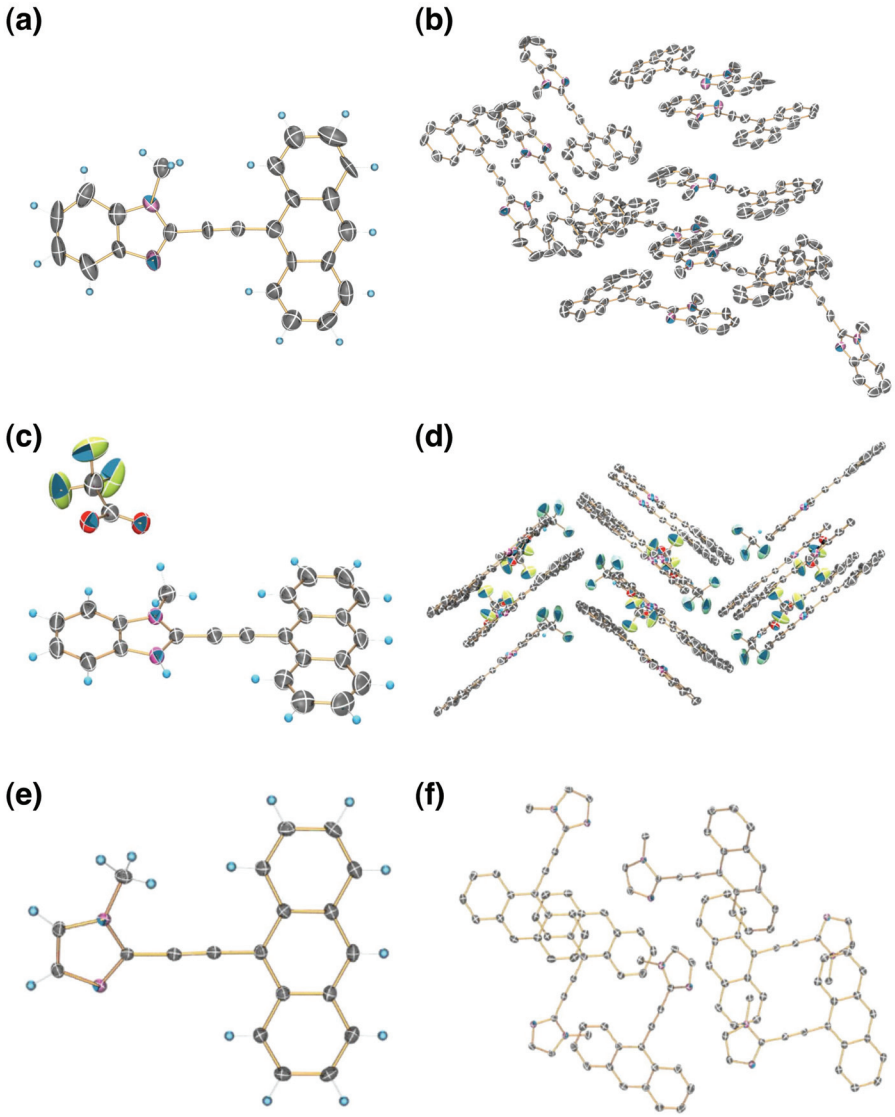


Fig. S6 ORTEP drawing (50% probability) of (a) BzIm-An, (c) BzIm-AnH$^+$, and (e) Im-An. Molecular packing diagram of the crystal structures of (b) BzIm-An, (d) BzIm-AnH$^+$, and (f) Im-An. Hydrogen atoms are omitted for clarity. Color code: blue sphere, H; gray sphere, C; purple sphere, N; red sphere, O; yellow sphere, F; green sphere, Cl.

Table S7 Crystallographic parameters and refinement details for BzIm-An, $(BzIm\text{-}An)_2$, $BzIm\text{-}AnH^+$, and Im-An.

	BzIm-An	$(BzIm\text{-}An)_2$	$BzIm\text{-}AnH^+$	Im-An
formula sum	$C_{24}H_{16}N_2$	$C_{49.80}H_{32.80}N_4Cl_{5.40}$	$C_{27}H_{18}N_2O_2F_3Cl_3$	$C_{20}H_{14}N_2$
formula weight	332.40	878.68	565.81	282.34
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1$ (#4)	P-1 (#2)	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a (Å)	27.6092(8)	10.4789(6)	12.2502(6)	18.3911(6)
b (Å)	7.5411(3)	15.0708(10)	8.3937(3)	7.4026(3)
c (Å)	40.9745(12)	15.5337(10)	24.8128(8)	21.2295(8)
α (deg)	90.00	70.0738(17)	90.00	90.00
β (deg)	92.2675(9)	76.6424(17)	95.8175(14)	91.5725(10)
γ (deg)	90.00	69.9763(16)	90.00	90.00
V (Å^3)	8524.4(4)	2148.6(2)	2538.23(17)	2889.15(18)
Z	20	2	4	8
F_{000}	3480.00	902.80	1152.00	1184.00
ρ_{calcd} (g cm^{-3})	1.295	1.358	1.481	1.298
μ (mm^{-1})	0.076	0.403	0.411	0.077
total no. of reflns	64980	17823	24666	22758
no. of independent reflns	6701	5020	4200	5264
parameters	2510	575	352	398
R1 [$I > 2\sigma(I)$]	0.0450	0.0659	0.0795	0.0327
wR2 [$I > 2\sigma(I)$]	0.0539	0.0832	0.109	0.0944
goodness of fit	0.917	1.068	0.985	1.086

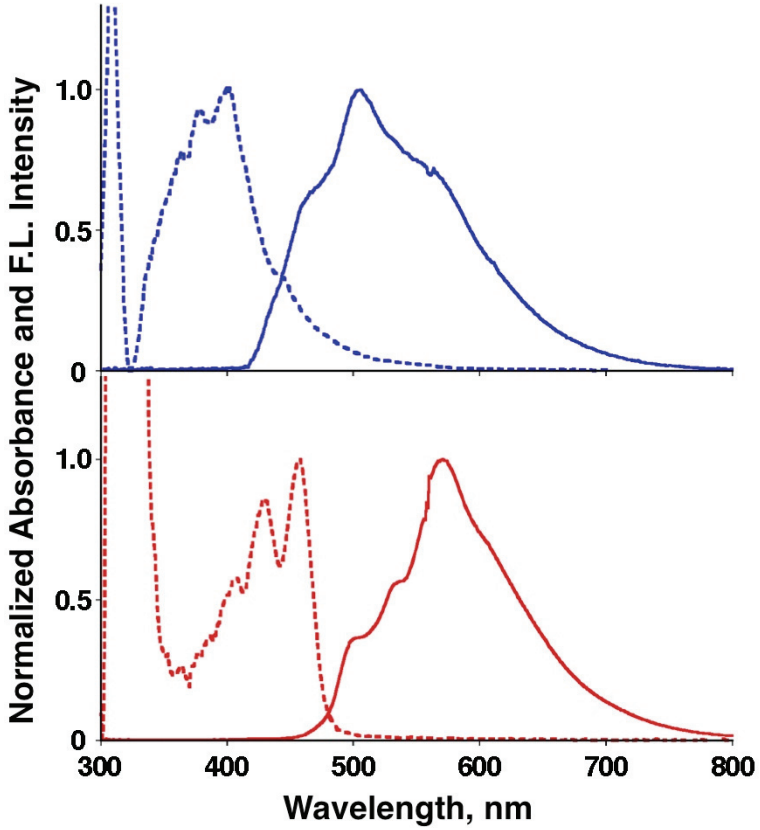


Fig. S8 Solid-state UV-vis absorption (dashed line) and fluorescence (solid line) spectra of $(BzIm\text{-}An)_2$ (top) and BzIm-An (bottom).