Sequential halochromic/mechanochromic luminescence of pyridyl-substituted solid-state emissive dyes: thermally controlled stepwise recovery of the original emission color

Suguru Ito,* Chika Nishimoto and Sayaka Nagai

*E-mail: suguru-ito@ynu.ac.jp

ᵃ Department of Advanced Materials Chemistry, Graduate School of Engineering,

Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

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1. Single-crystal X-ray diffraction analyses

X-ray analysis of 1

A single crystal of **1** was obtained from vapor diffusion of hexane into a chloroform/DMF solution of **1** and was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-Kα radiation (λ = 1.54184 Å). The data were collected at a temperature of −50 ± 1 °C to a maximum 2θ value of 150.5°. A total of 2786 oscillation images were collected. The crystal-to-detector distance was 40.00 mm. Readout was performed in the 0.172 mm pixel mode.

Of the 25682 reflections that were collected, 4448 were unique (R_{int} = 0.0301); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[1] The linear absorption coefficient, μ, for Cu-Kα radiation is 14.374 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.654 to 0.826. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[3] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[4]

Crystal data for **1** (CCDC 1935319): $C_{32}H_{19}N_5S$, M = 505.60, monoclinic, a = 9.71088(5) Å, b = 16.39216(9) Å, c = 15.37234(9) Å, β = 97.2646(5)°, V = 2427.36(2) Å^3, space group $P2_1/n$ (no. 14), Z = 4, D_c = 1.383 g cm^{-3}, $F(000)$ = 1048.00, T = 223(1) K, μ(Cu-Ka) = 14.374 cm^{-1}, 25682 reflections measured, 4448 independent (R_{int} = 0.0301). The final refinement converged to R_1 = 0.0346 for I > 2.0$\sigma(I)$, wR_2 = 0.0919 for all data.
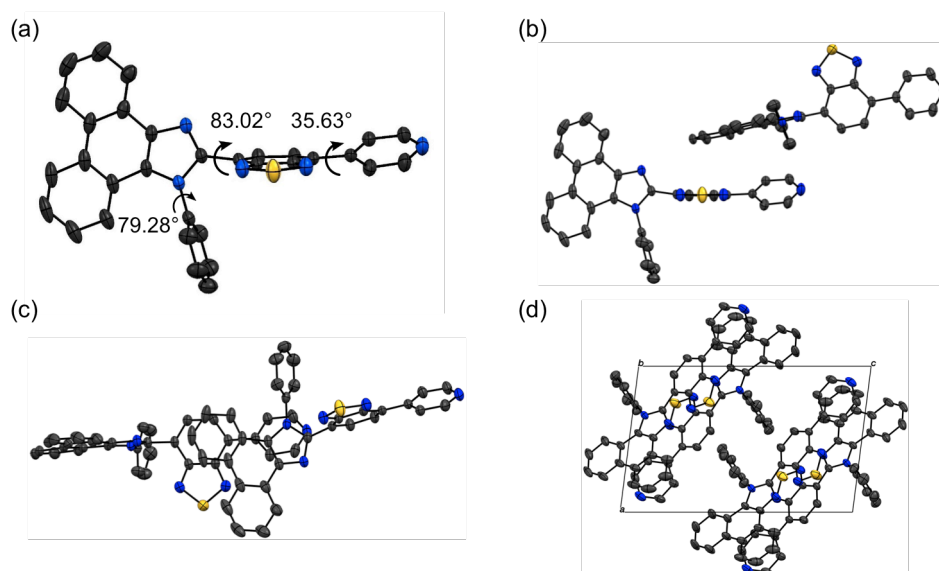

Fig. S1 The molecular structure of **1** with atomic displacement parameters set at 50% probability (Color code: gray = C, blue = N, yellow = S). All hydrogen atoms are omitted for clarity. (a) Front view. (b) Side view of neighbouring two molecules. (c) Top view of neighbouring two molecules. (d) Unit cell structure viewed along *b*-axis.

A single crystal of **1·2a** was obtained from vapor diffusion of hexane into a chloroform solution of a 1:1 molar mixture of **1** and **2a** and was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using graphite monochromated Cu-Kα radiation (λ = 1.54184 Å). The data were collected at a temperature of -50 ± 1 °C to a maximum 2θ value of 152.2°. A total of 3032 oscillation images were collected. The crystal-to-detector distance was 40.00 mm. Readout was performed in the 0.172 mm pixel mode.

Of the 33807 reflections that were collected, 5609 were unique (R_{int} = 0.0471); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[1] The linear absorption coefficient, μ, for Cu-Kα radiation is 12.956 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.570 to 0.768. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The positions of hydrogen atoms of carboxy groups were localized from the differential Fourier synthesis. All calculations were performed using the CrystalStructure[3] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[4]

Crystal data for **1·2a** (CCDC 1935320): $C_{39}H_{25}N_5O_2S$, M = 627.72, monoclinic, a = 9.93969(8) Å, b = 17.64482(16) Å, c = 17.57204(14) Å, β = 93.1282(8)°, V = 3077.26(4) Å^3, space group $P2_1/n$ (no. 14), Z = 4, D_c = 1.355 g cm^{-3}, $F(000)$ = 1304.00, T = 223(1) K, μ(Cu-Ka) = 12.956 cm^{-1}, 33807 reflections measured, 5609 independent (R_{int} = 0.0471). The final refinement converged to R_1 = 0.0355 for $I > 2.0\sigma(I)$, wR_2 = 0.0942 for all data.
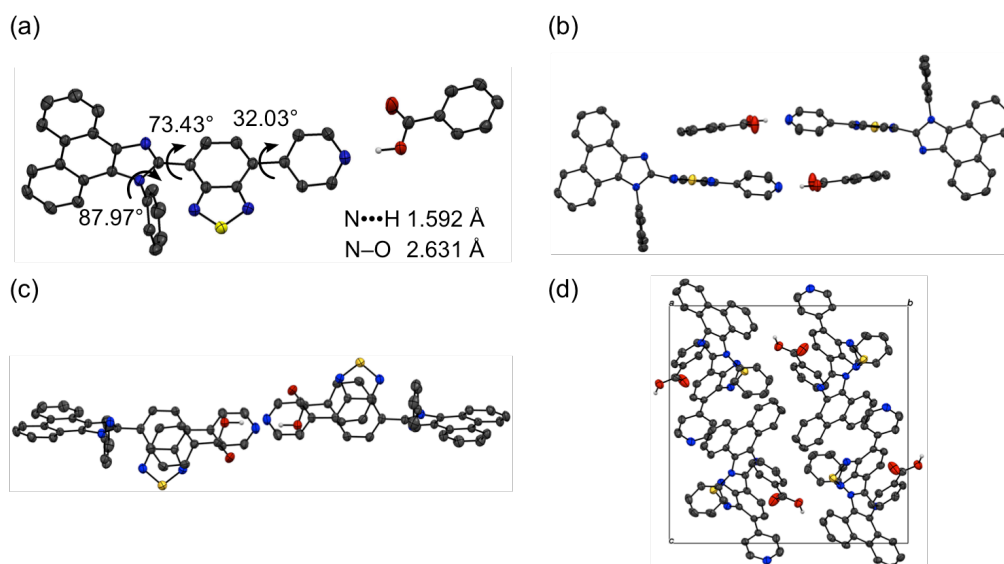

Fig. S2 The molecular structure of **1·2a** with atomic displacement parameters set at 50% probability (Color code: gray = C, red = O, blue = N, yellow = S). All hydrogen atoms except for carboxy group are omitted for clarity. (a) Front view. (b) Side view of neighbouring two complexes. (c) Tope view of neighbouring two complexes. (d) Unit cell structure viewed along *a*-axis.

A single crystal of **1•2b** was obtained from vapor diffusion of hexane into a chloroform solution of a 1:1 molar mixture of **1** and **2b** and was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using graphite monochromated Cu-Kα radiation (λ = 1.54184 Å). The data were collected at a temperature of −50 ± 1 °C to a maximum 2θ value of 150.4°. A total of 4052 oscillation images were collected. The crystal-to-detector distance was 40.00 mm. Readout was performed in the 0.172 mm pixel mode.

Of the 47704 reflections that were collected, 5951 were unique (R_{int} = 0.0425); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[1] The linear absorption coefficient, μ, for Cu-Kα radiation is 14.217 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.721 to 0.872. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The positions of hydrogen atoms of carboxy groups were localized from the differential Fourier synthesis. All calculations were performed using the CrystalStructure[3] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[4]

Crystal data for **1•2b** (CCDC 1935321): $C_{40}H_{24}F_3N_5O_2S$, M = 695.72, monoclinic, a = 10.12758(5) Å, b = 16.68174(10) Å, c = 19.48203(10) Å, β = 99.0942(5)°, V = 3250.03(3) Å^3, space group $P2_1/n$ (no. 14), Z = 4, D_c = 1.422 g cm^{-3}, $F(000)$ = 1432.00, T = 223(1) K, μ(Cu-Ka) = 14.217 cm^{-1}, 47704 reflections measured, 5951 independent (R_{int} = 0.0425). The final refinement converged to R_1 = 0.0568 for $I > 2.0\sigma(I)$, wR_2 = 0.1623 for all data.

(a)

74.85° 27.49°

83.95°

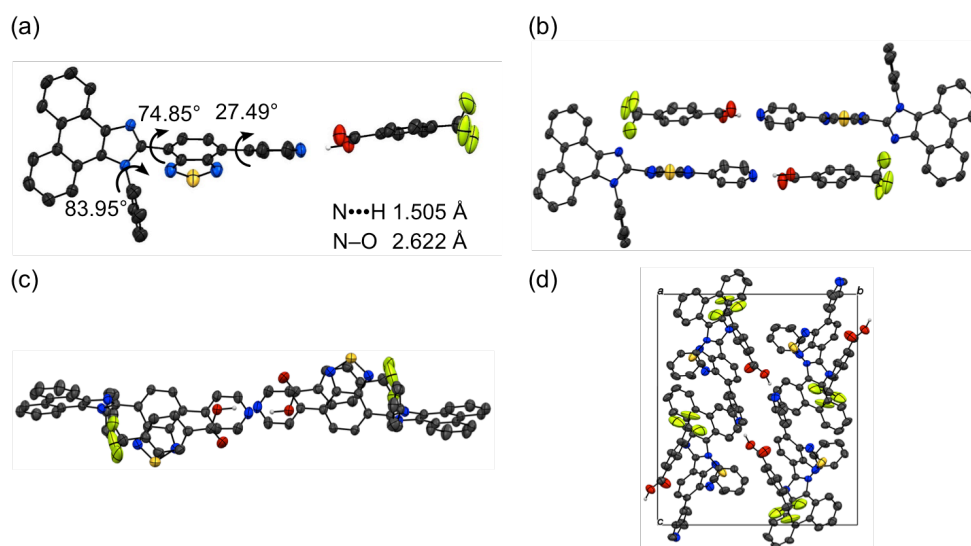N•••H 1.505 Å
N–O 2.622 Å

(b)

(c)

(d)

Fig. S3 The molecular structure of **1•2b** with atomic displacement parameters set at 50% probability (Color code: gray = C, red = O, blue = N, yellow = S, green = F). All hydrogen atoms except for carboxy group are omitted for clarity. (a) Front view. (b) Side view of neighbouring two complexes. (c) Tope view of neighbouring two complexes. (d) Unit cell structure viewed along *a*-axis.

A single crystal of **1•2c** was obtained from vapor diffusion of hexane into a chloroform solution of a 1:1 molar mixture of **1** and **2c** and was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using graphite monochromated Cu-Kα radiation (λ = 1.54184 Å). The data were collected at a temperature of -50 ± 1 °C to a maximum 2θ value of 150.6°. A total of 2916 oscillation images were collected. The crystal-to-detector distance was 40.00 mm. Readout was performed in the 0.172 mm pixel mode.

Of the 34401 reflections that were collected, 5741 were unique (R_{int} = 0.0333); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[1] The linear absorption coefficient, μ, for Cu-Kα radiation is 13.041 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.696 to 0.795. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The positions of hydrogen atoms of carboxy groups were localized from the differential Fourier synthesis. All calculations were performed using the CrystalStructure[3] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[4]

Crystal data for **1•2c** (CCDC 1935322): $C_{40}H_{24}N_6O_2S$, M = 652.73, monoclinic, a = 9.72297(7) Å, b = 17.69375(11) Å, c = 18.28982(12) Å, β = 94.3128(6)°, V = 3137.59(4) Å^3, space group $P2_1/n$ (no. 14), Z = 4, D_c = 1.382 g cm^{-3}, $F(000)$ = 1352.00, T = 223(1) K, μ(Cu-Ka) = 13.041 cm^{-1}, 34401 reflections measured, 5741 independent (R_{int} = 0.0333). The final refinement converged to R_1 = 0.0357 for $I > 2.0\sigma(I)$, wR_2 = 0.0942 for all data.

(a)

73.35°   30.10°

82.25°

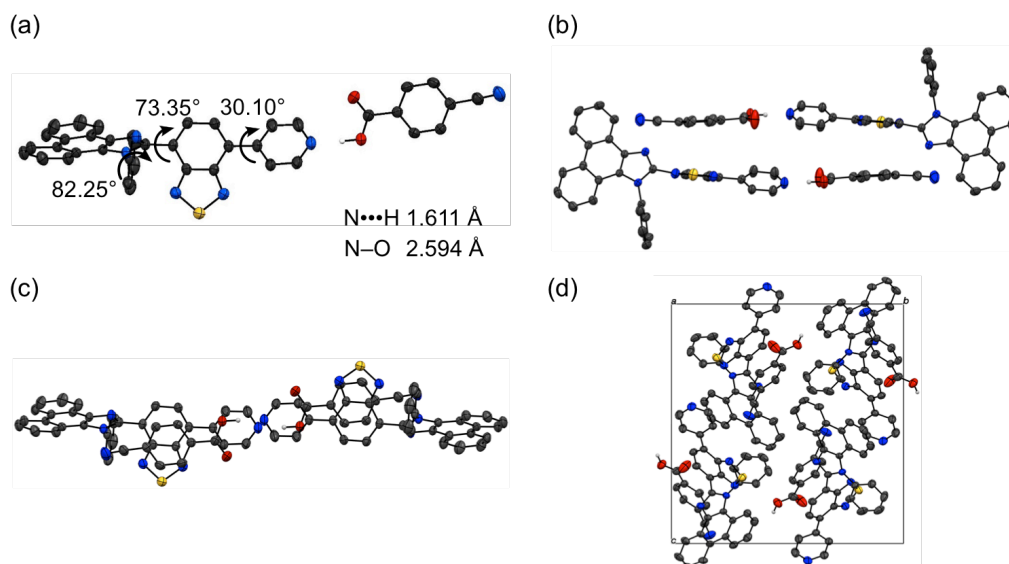N•••H 1.611 Å

N–O 2.594 Å

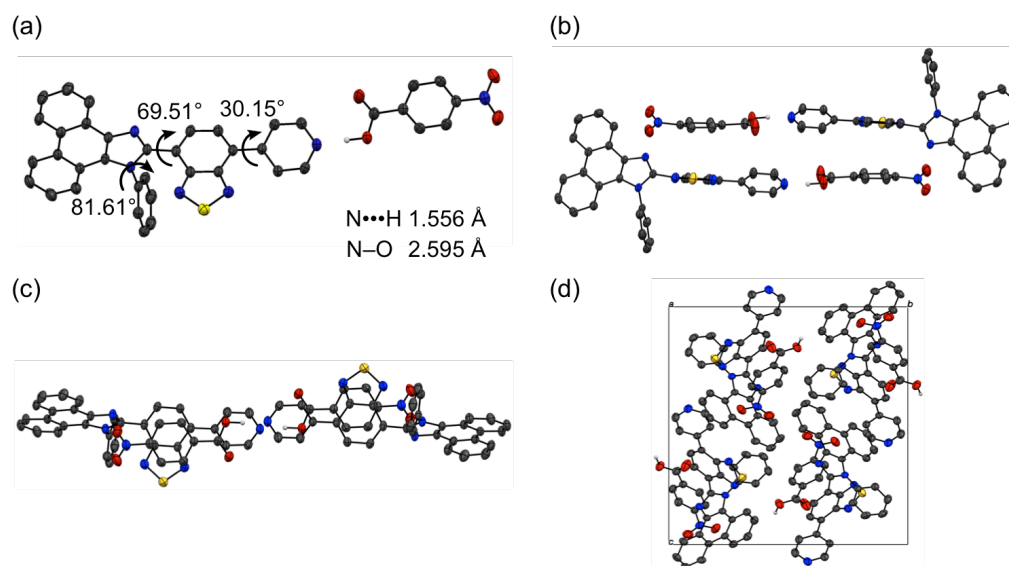(b)

(c)

(d)

Fig. S4 The molecular structure of **1•2c** with atomic displacement parameters set at 50% probability (Color code: gray = C, red = O, blue = N, yellow = S). All hydrogen atoms except for carboxy group are omitted for clarity. (a) Front view. (b) Side view of neighbouring two complexes. (c) Tope view of neighbouring two complexes. (d) Unit cell structure viewed along *a*-axis.

A single crystal of **1•2d** was obtained from vapor diffusion of hexane into a chloroform solution of a 1:1 molar mixture of **1** and **2d** and was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using graphite monochromated Cu-Kα radiation (λ = 1.54184 Å). The data were collected at a temperature of –50 ± 1 °C to a maximum 2θ value of 152.0°. A total of 3226 oscillation images were collected. The crystal-to-detector distance was 40.00 mm. Readout was performed in the 0.172 mm pixel mode.

Of the 36448 reflections that were collected, 5700 were unique (R_{int} = 0.0452); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[1] The linear absorption coefficient, μ, for Cu-Kα radiation is 13.822 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.284 to 0.643. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The positions of hydrogen atoms of carboxy groups were localized from the differential Fourier synthesis. All calculations were performed using the CrystalStructure[3] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[4]

Crystal data for **1•2d** (CCDC 1935323): C$_{39}$H$_{24}$N$_{6}$O$_{4}$S, M = 672.72, monoclinic, a = 9.74862(8) Å, b = 17.91753(15) Å, c = 17.82303(15) Å, β = 92.1261(8)°, V = 3111.03(4) Å^{3}, space group $P2_1/n$ (no. 14), Z = 4, D_c = 1.436 g cm^{-3}, $F(000)$ = 1392.00, T = 223(1) K, μ(Cu-Ka) = 13.822 cm^{-1}, 36448 reflections measured, 5700 independent (R_{int} = 0.0452). The final refinement converged to R_1 = 0.0389 for $I > 2.0\sigma(I)$, wR_2 = 0.1062 for all data.

Fig. S5 The molecular structure of **1•2d** with atomic displacement parameters set at 50% probability (Color code: gray = C, red = O, blue = N, yellow = S). All hydrogen atoms except for carboxy group are omitted for clarity. (a) Front view. (b) Side view of neighbouring two complexes. (c) Tope view of neighbouring two complexes. (d) Unit cell structure viewed along a-axis.
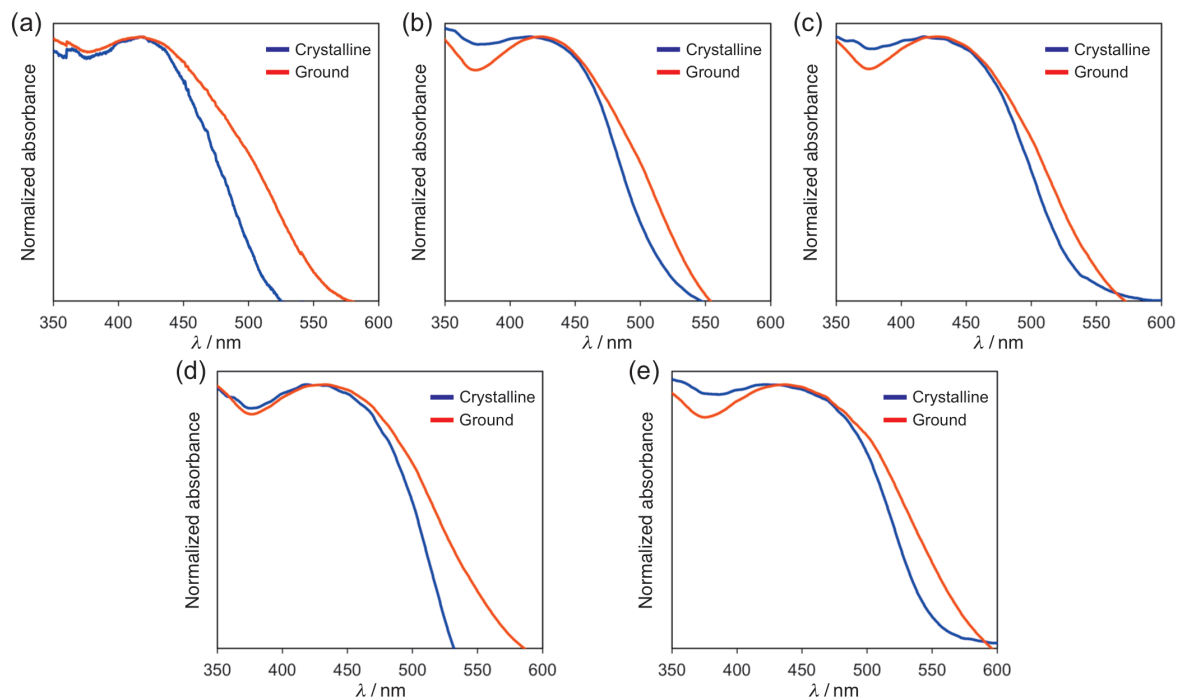
2. Absorption spectra

Fig. S6 Solid-state absorption spectra of crystalline and ground **1** (a), **1·2a** (b), **1·2b** (c), **1·2c** (d), and **1·2d** (e).
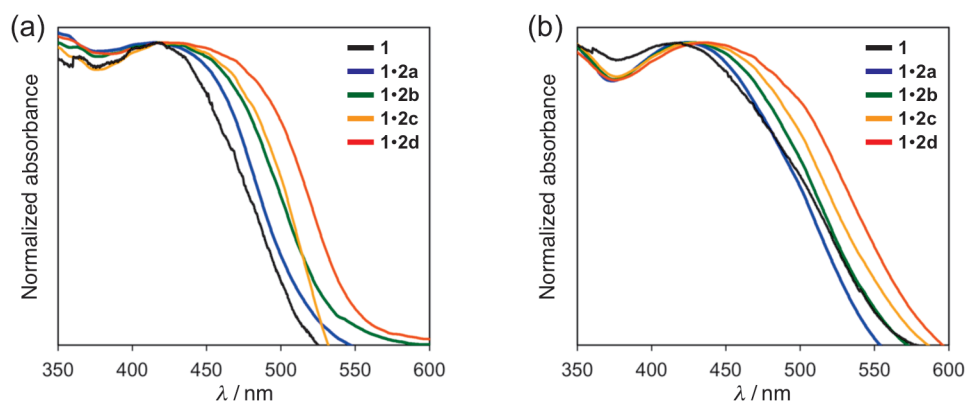

Fig. S7 Solid-state absorption spectra of (a) crystalline and (b) ground **1** and **1·2a–d**.

3. Theoretical calculations

Based on the single-crystal X-ray diffraction structures, absorption wavelengths of **1** in **1•2a–d** and discrete hydrogen-bond-forming complexes **1•2a–d** were calculated by time-dependent density functional theory (TD-DFT) at the CAM-B3LYP/6-31G(d) level of theory (Table S1).

Table S1 Experimental absorption maxima and calculated absorption properties of **1a–f**.

Compd	Absorption in crystal λ_{abs} (nm)	Calcd absorption λ_{abs} (nm)	Transition from HOMO to LUMO	Oscillator strength	HOMO (eV)	LUMO (eV)	Dipole moment (D)
1	417	355.82	0.68612	0.0260	−6.65	−1.47	4.5684
1(•2a)		366.65	0.66808	0.1687	−6.61	−1.50	4.4719
1•2a	415	379.96	0.67844	0.1542	−6.70	−1.74	6.3147
1•(2b)		362.65	0.67160	0.1459	−6.64	−1.49	4.3196
1•2b	417	382.77	0.68249	0.1248	−6.78	−1.86	9.2723
1•(2c)		371.73	0.66515	0.2196	−6.60	−1.51	4.3534
1•2c	419	386.76	0.67679	0.2087	−6.74	−1.82	10.2904
1•(2d)		368.35	0.66025	0.2450	−6.63	−1.50	4.3407
1•2d	422	385.37	0.67547	0.2295	−6.79	−1.86	11.1922
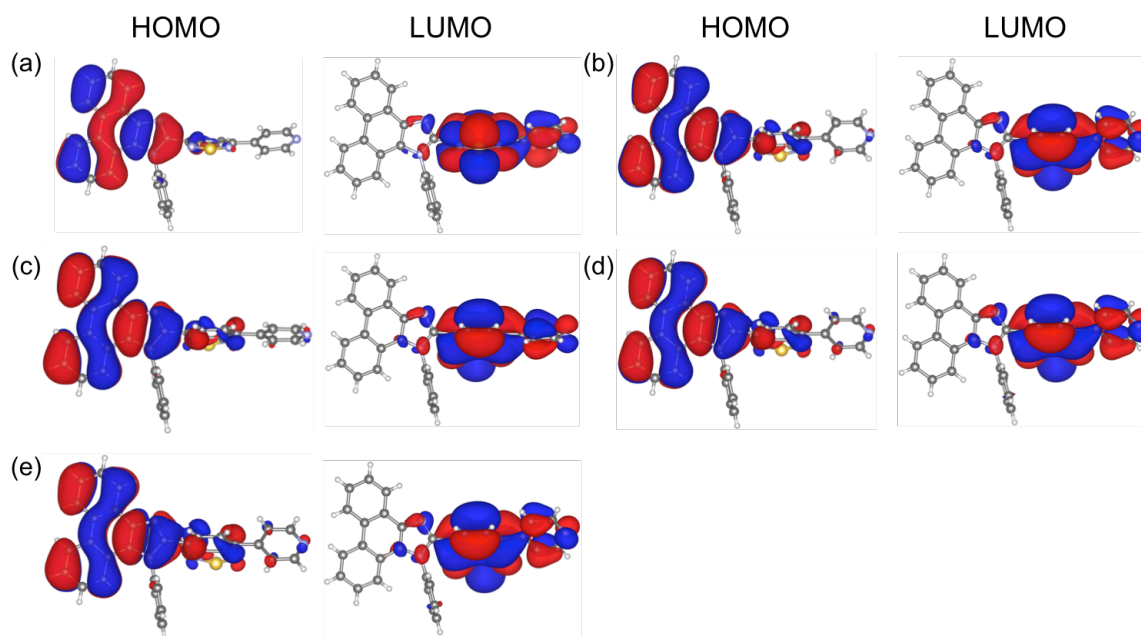
Fig. S8 HOMO and LUMO of **1** (a), **1•(2a)** (b), **1(•2b)** (c), **1(•2c)** (d), and **1(•2d)** (e) calculated at the CAM-B3LYP/6-31G(d) level. The structures are drawn by VESTA.[5]

	HOMO	LUMO

(a)

(b)

(c)

(d)
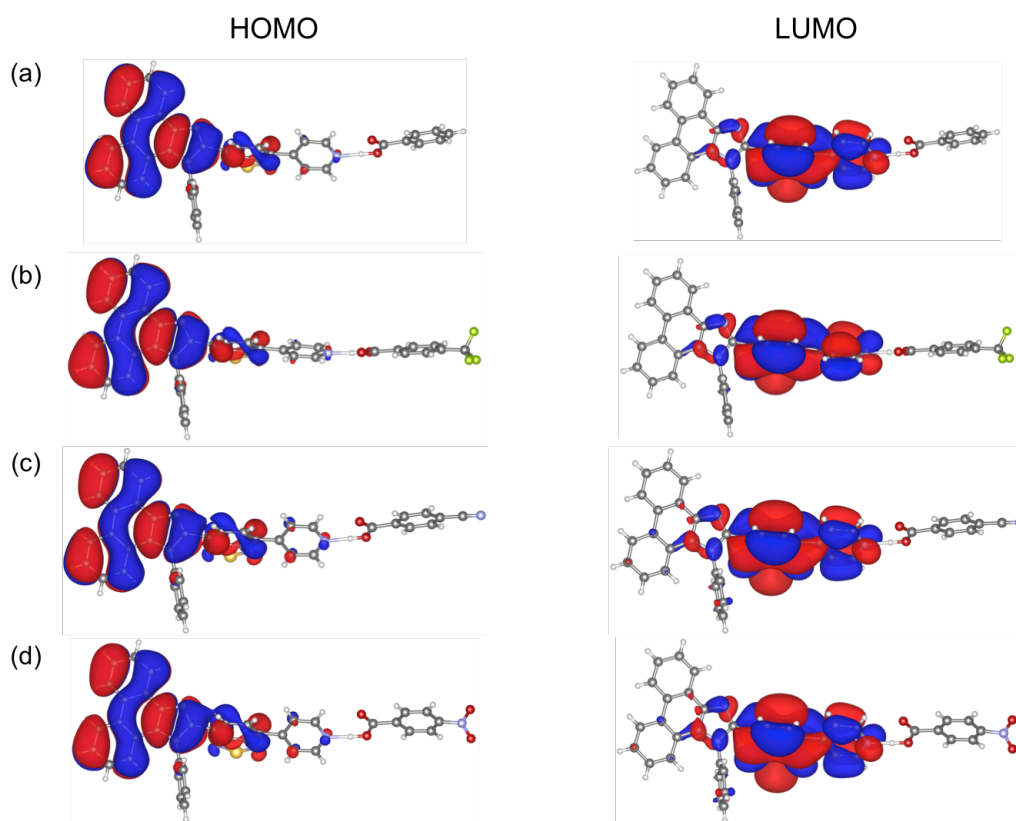
Fig. S9 HOMO and LUMO of **1·2a** (a), **1·2b** (b), **1·2c** (c), and **1·2d** (d) calculated at the CAM-B3LYP/6-31G(d) level. The structures are drawn by VESTA.[5]

4. ^{1}H NMR spectrum of 1 after heating 1•2a–d

^{1}H NMR analyses revealed the absence of benzoic acid derivatives **2a–d** after heating **1•2a–d** to 185–260 °C (Fig. S10–S13).
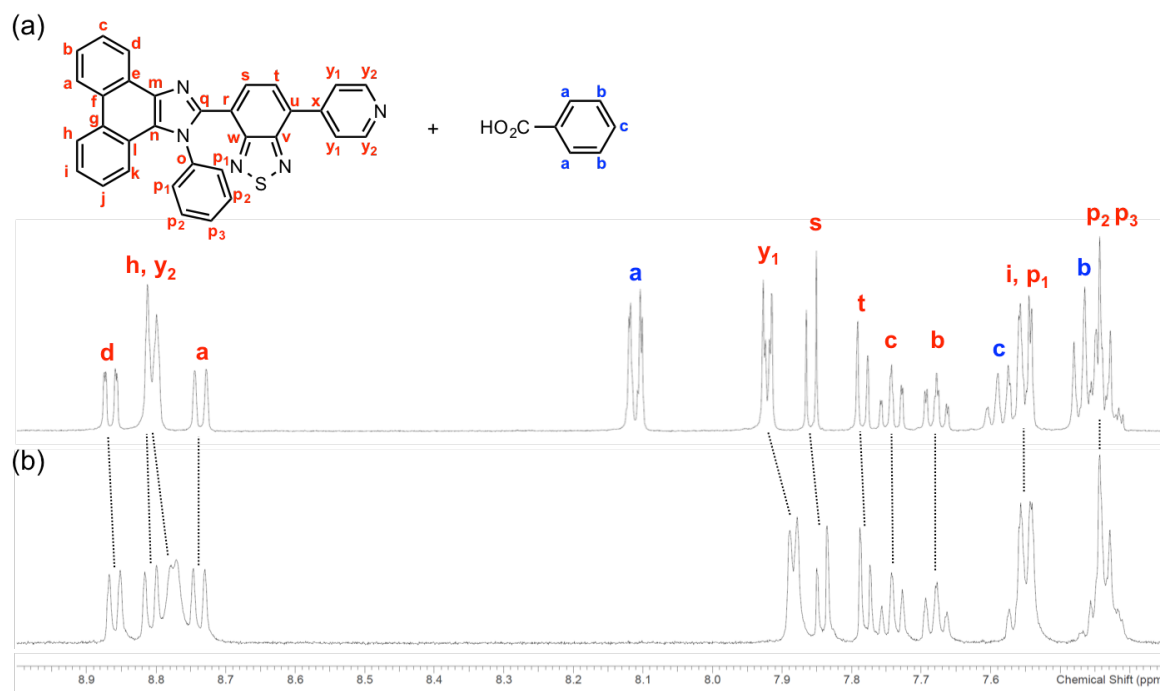

Fig. S10 ^{1}H NMR spectra of (a) crystalline **1•2a** and (b) crystalline **1** obtained after heating **1•2a** (500 MHz, in CDCl$_3$).
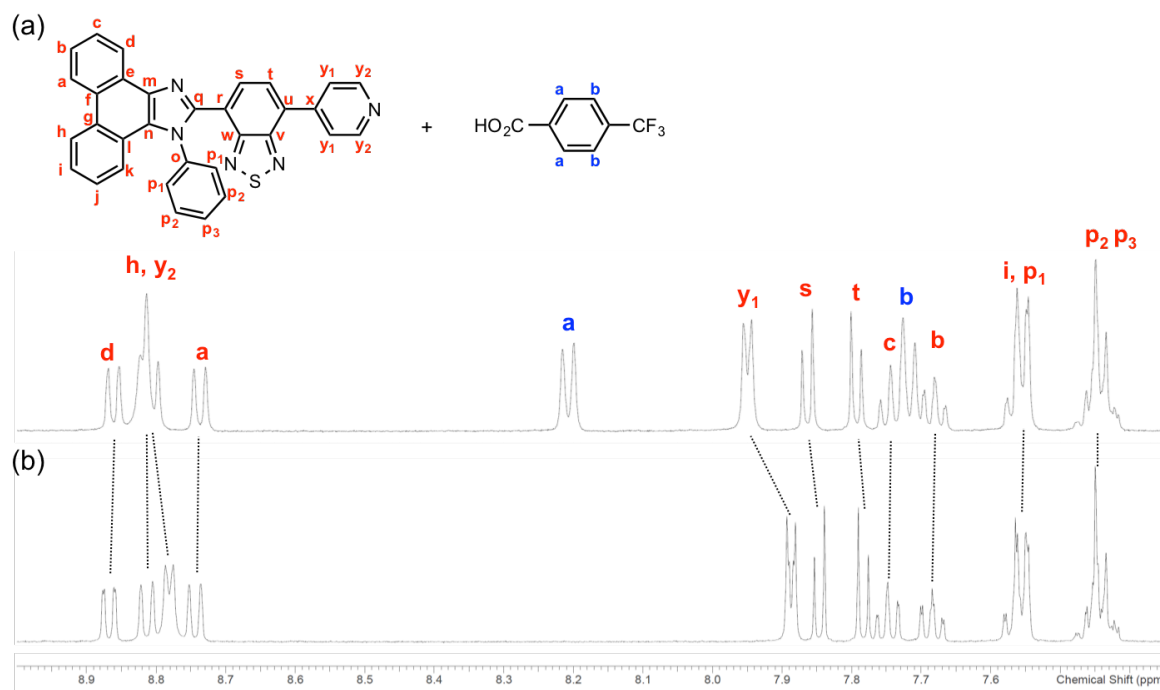
Fig. S11 ^{1}H NMR spectra of (a) crystalline **1•2b** and (b) crystalline **1** obtained after heating **1•2b** (500 MHz, in CDCl$_3$).
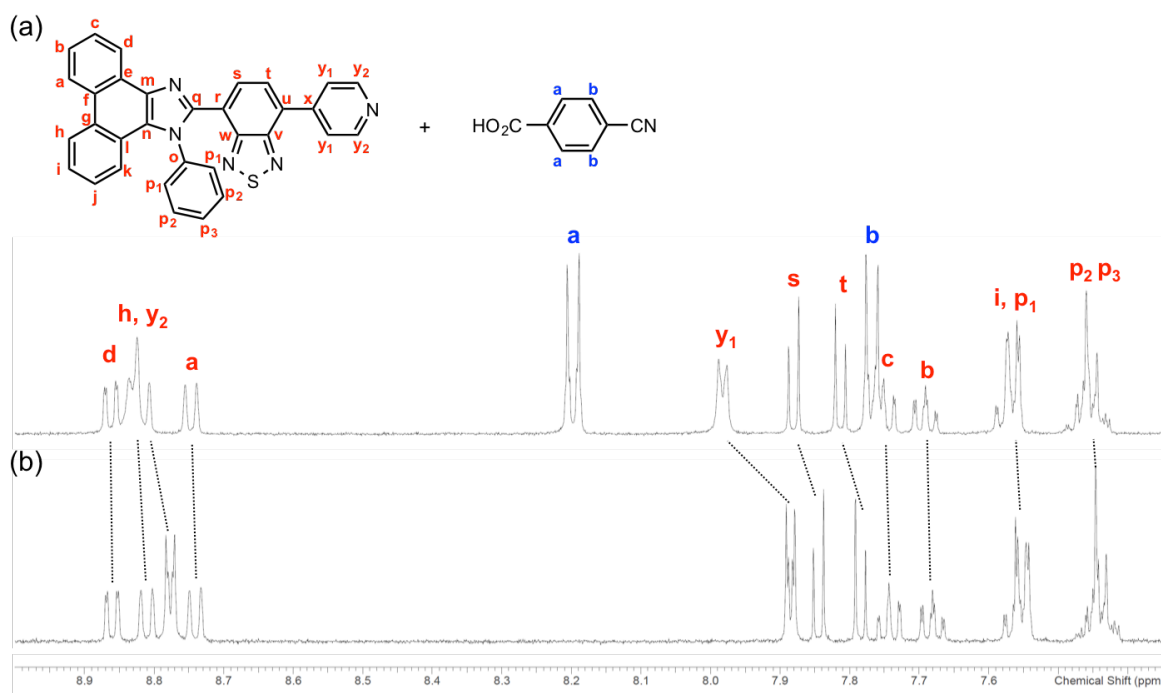
Fig. S12 ^{1}H NMR spectra of (a) crystalline **1•2c** and (b) crystalline **1** obtained after heating **1•2c** (500 MHz, in CDCl$_3$).
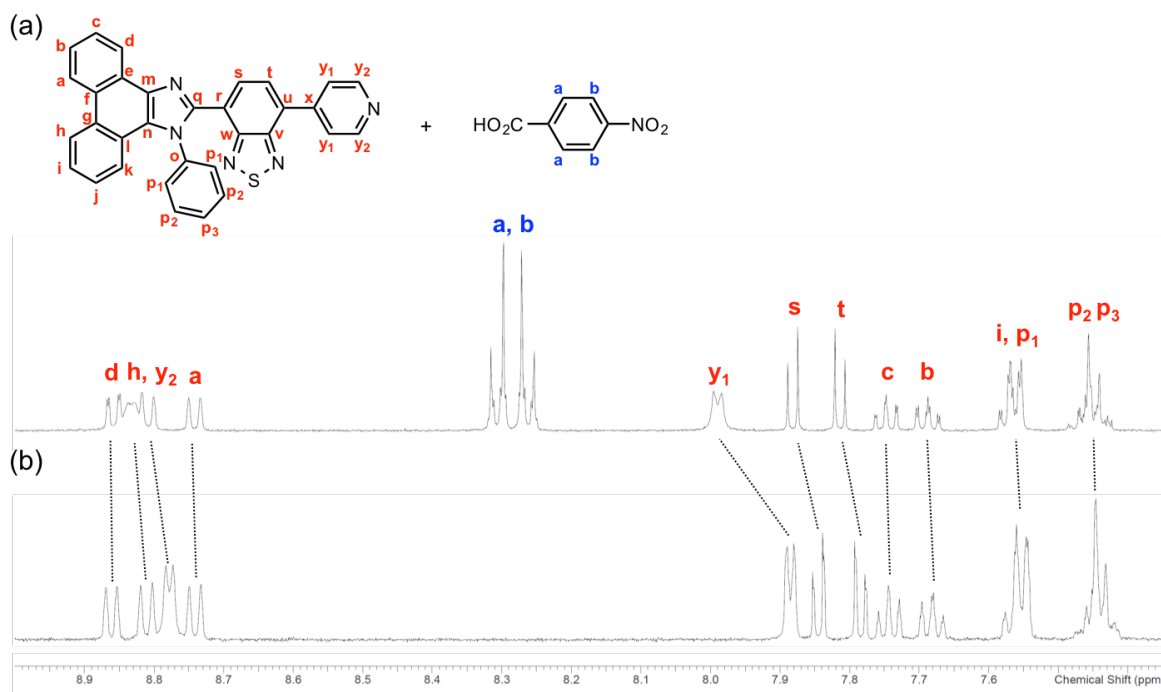
Fig. S13 ^{1}H NMR spectra of (a) crystalline **1•2d** and (b) crystalline **1** obtained after heating **1•2d** (500 MHz, in CDCl$_3$).
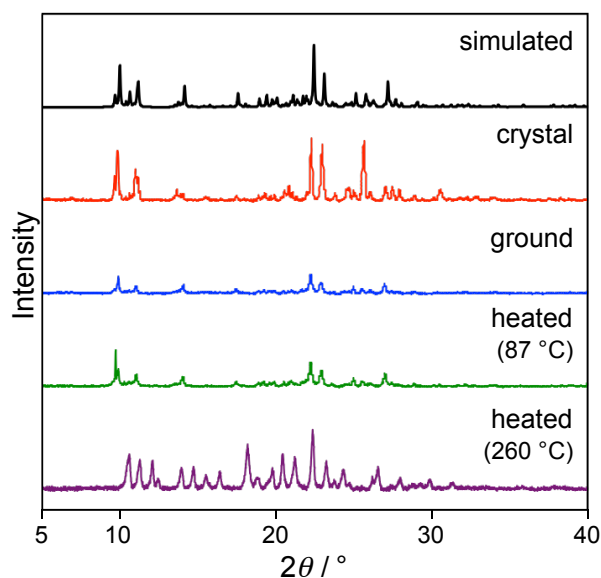
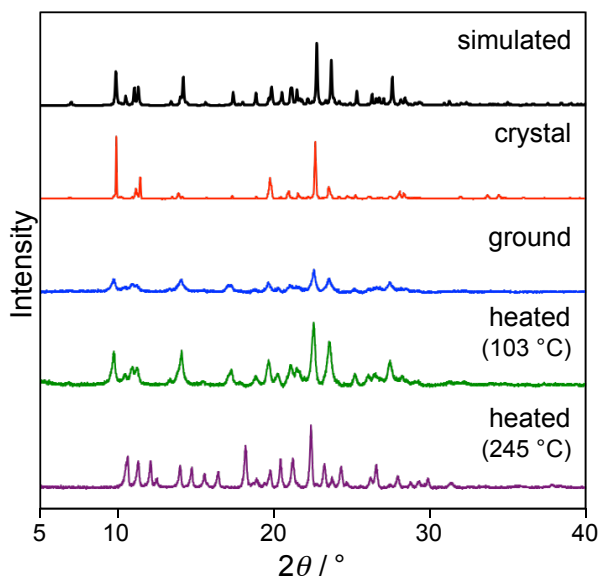## 5. Powder X-ray diffraction analyses of 1•2b–d
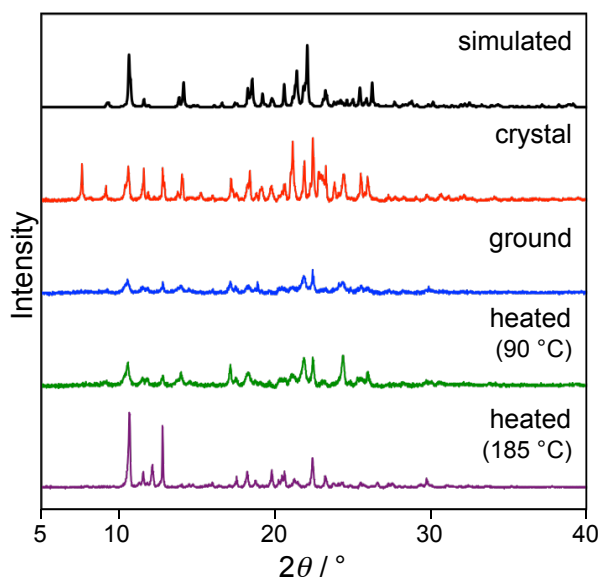
Fig. S14 PXRD patterns for **1•2b**. Black line: Simulated PXRD pattern calculated from the single-crystal structure. Red line: Experimental PXRD pattern of the powdered crystalline sample. Blue line: Experimental PXRD pattern of the ground sample. Green line: Experimental PXRD pattern of the sample after heating to 90 °C. Purple line: Experimental PXRD pattern of the sample after heating to 185 °C.

Fig. S15 PXRD patterns for **1•2c**. Black line: Simulated PXRD pattern calculated from the single-crystal structure. Red line: Experimental PXRD pattern of the powdered crystalline samples. Blue line: Experimental PXRD pattern of the ground sample. Green line: Experimental PXRD pattern of the sample after heating to 87 °C. Purple line: Experimental PXRD pattern of the sample after heating to 260 °C.

Fig. S16 PXRD patterns for **1•2d**. Black line: Simulated PXRD pattern calculated from the single-crystal structure. Red line: Experimental PXRD pattern of the powdered crystalline sample. Blue line: Experimental PXRD pattern of the ground sample. Green line: Experimental PXRD pattern of the sample after heating to 103 °C. Purple line: Experimental PXRD pattern of the sample after heating to 245 °C.

6. Differential scanning calorimetry (DSC) analyses

In the DSC thermograms of **1·2b–d**, endothermic peaks that correspond to the vaporization of **2b–d** (T_v) and the melting points of **1** (T_m) were observed for crystalline samples, and cold crystallization transition peaks (T_c) followed by T_v and T_m were observed for ground samples (Fig. S17–S19).
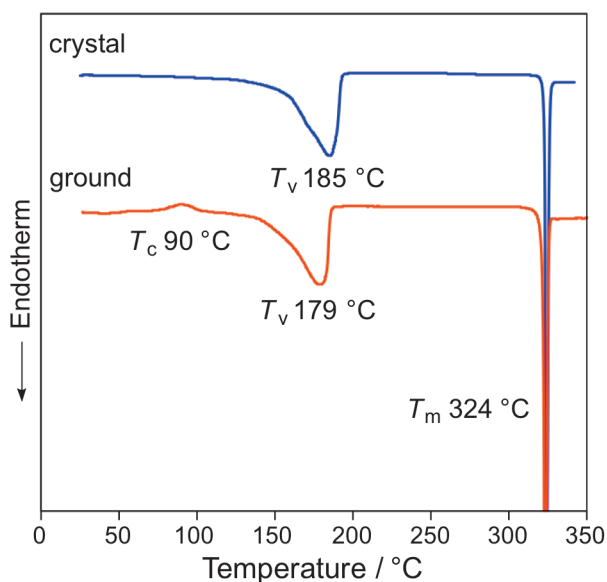
Fig. S17 DSC thermograms of **1·2b** for powdered crystalline sample (blue line) and ground sample (red sample). T_v, T_c, and T_m values are noted near the corresponding peaks.
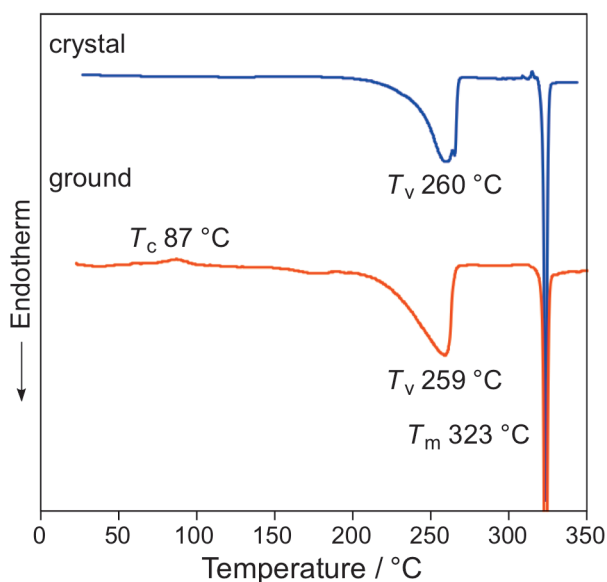
Fig. S18 DSC thermograms of **1·2c** for powdered crystalline sample (blue line) and ground sample (red sample). T_v, T_c, and T_m values are noted near the corresponding peaks.
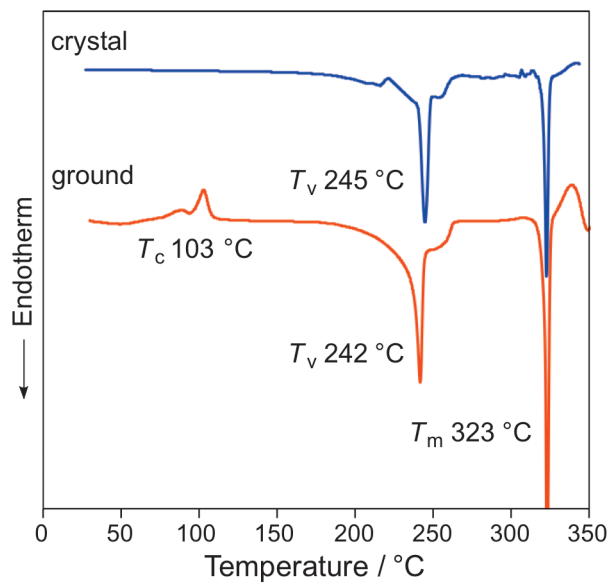
Fig. S19 DSC thermograms of **1·2d** for powdered crystalline sample (blue line) and ground sample (red sample). T_v, T_c, and T_m values are noted near the corresponding peaks.

7. Powder X-ray diffraction analyses of 4/2a–d

PXRD analyses of the mixture **4**/**2a** indicated that both **4** and **2a** exist as amorphous states (Fig. S20). No diffraction peak attributed to **4** was observed by PXRD analyses of **4**/**2b**–**d**, although trace diffraction peaks of crystalline **2b**–**d** were detected probably due to the higher crystallinity of **2b**–**d** than **2a** (Fig. S21–S23).
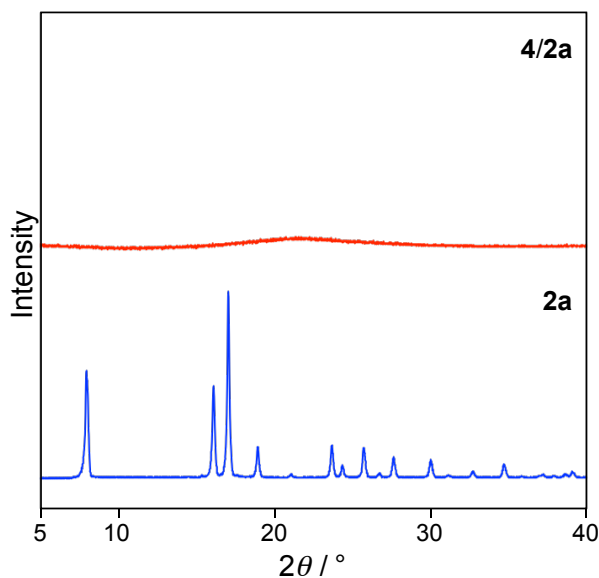
Fig. S20 PXRD patterns for **4**/**2a** and **2a**. Red line: Experimental PXRD pattern of the powdered mixture of **4**/**2a**. Blue line: Experimental PXRD pattern of the crystalline sample of **2a**.
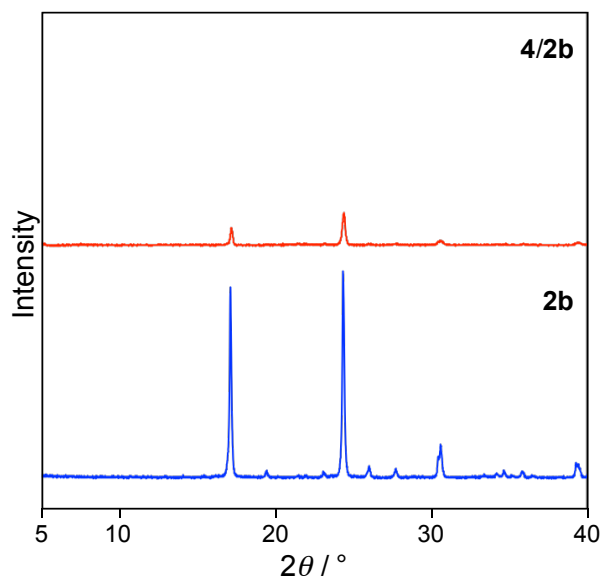
Fig. S21 PXRD patterns for **4**/**2b** and **2b**. Red line: Experimental PXRD pattern of the powdered mixture of **4**/**2b**. Blue line: Experimental PXRD pattern of the crystalline sample of **2b**.
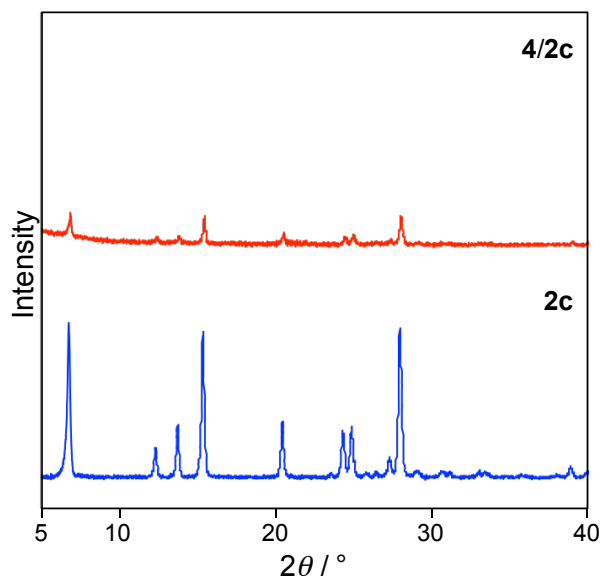
Fig. S22 PXRD patterns for **4/2c** and **2c**. Red line: Experimental PXRD pattern of the powdered mixture of **4/2c**. Blue line: Experimental PXRD pattern of the crystalline sample of **2c**.
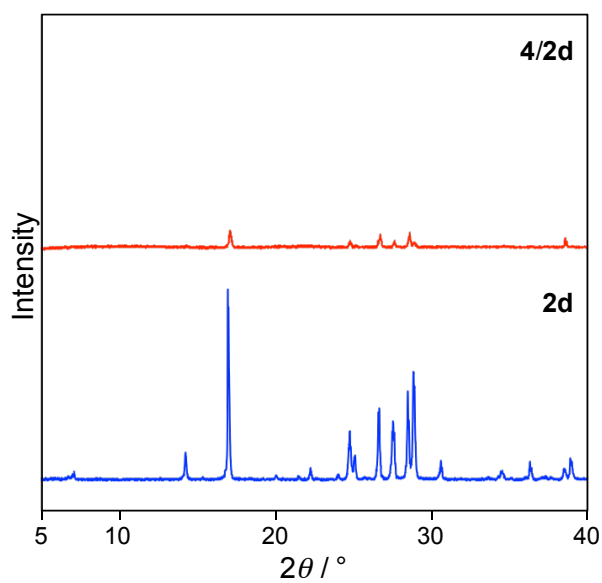

Fig. S23 PXRD patterns for **4/2d** and **2d**. Red line: Experimental PXRD pattern of the powdered mixture of **4/2d**. Blue line: Experimental PXRD pattern of the crystalline sample of **2d**.

8. References

1) CrysAlisPro: Data Collection and Processing Software, Rigaku Corporation (2015). Tokyo 196-8666, Japan.

2) SIR2011: M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 2012, **45**, 357.

3) CrystalStructure 4.2.5: Crystal Structure Analysis Package, Rigaku Corporation (2000-2017). Tokyo 196-8666, Japan.

4) SHELXL Version 2014/7: G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

5) K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272.
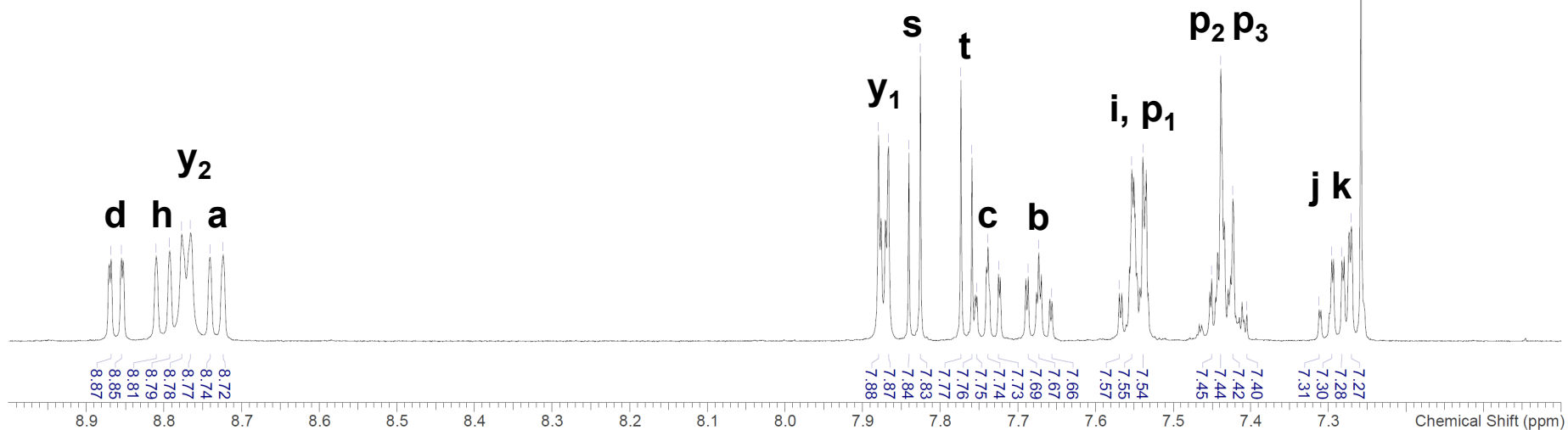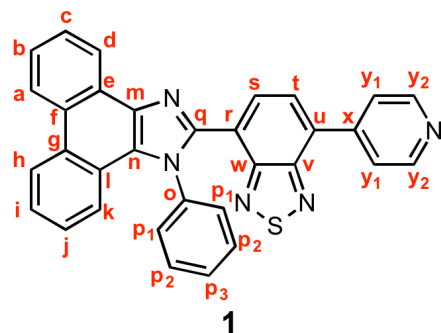
^{1}H NMR spectrum of **1** (500 MHz, in CDCl$_3$, rt)

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Original Points Count	32768	Owner	root	PC	1	PROBHD	⟨5 mm BBO BB-1H Z-GRD Z859001/0006 ⟩		
PULPROG	⟨zg30⟩	Points Count	32768	Pulse Sequence	zg30	Receiver Gain	456.10	SF	500.130006648269
SFO1	500.133088507478			SI	32768	SSB	0	SW(cyclical) (Hz)	10330.58
SWH	10330.5785123967			Solvent	CHLOROFORM-d			Spectrum Offset (Hz)	3074.6074
Spectrum Type	standard	Sweep Width (Hz)	10330.26	TD	65536	TD0	1	TE	298.9
Temperature (degree C)	25.900	WDW	1						

Desktop.001.001.1r.esp

S19
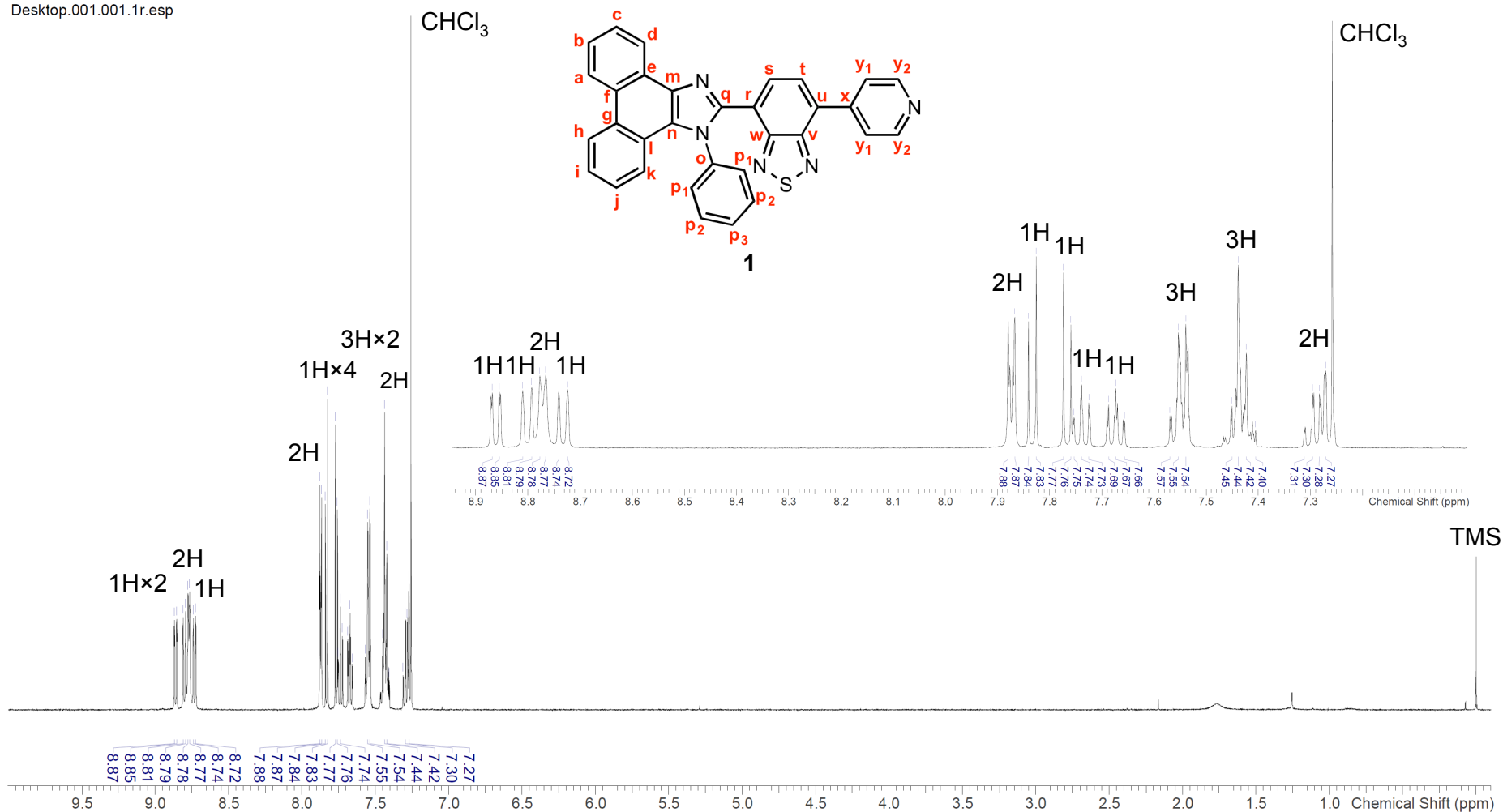
Partial ^{1}H NMR spectrum of **1** (500 MHz, in CDCl$_3$, rt)

Acquisition Time (sec)	3.1719	Comment	1125–2+H	D	3.827959	D1	3.827959	DE	6
DS	2	Date	25 Jan 2019 21:23:43			Date Stamp	25 Jan 2019 21:23:43		
File Name	C:¥Users¥Asami–Lab¥Desktop¥1¥PDATA¥1¥1r			Frequency (MHz)	500.1300	GB	0	INSTRUM	<spect>
LB	0.1	NS	8	Nucleus	1H	Number of Transients	8	Origin	spect
Original Points Count	32768	Owner	root	PC	1	PROBHD	<5 mm BBO BB–1H Z–GRD Z859001/0006 >		
PULPROG	<zg30>	Points Count	32768	Pulse Sequence	zg30	Receiver Gain	456.10	SF	500.130006648269
SFO1	500.133088507478			SI	32768	SSB	0	SW(cyclical) (Hz)	10330.58
SWH	10330.5785123967			Solvent	CHLOROFORM–d			Spectrum Offset (Hz)	3074.6074
Spectrum Type	standard	Sweep Width (Hz)	10330.26	TD	65536	TD0	1	TE	298.9
Temperature (degree C)	25.900	WDW	1						

S20

^{13}C NMR spectrum of **1** (126 MHz, in CDCl$_3$, rt)

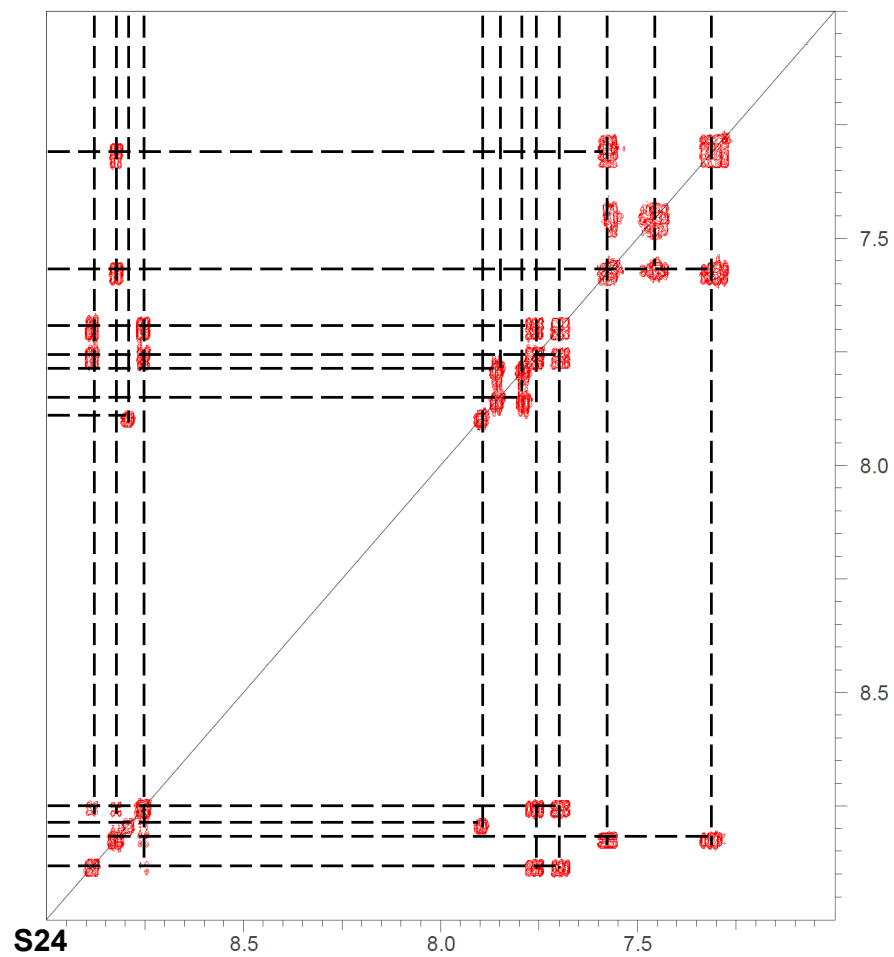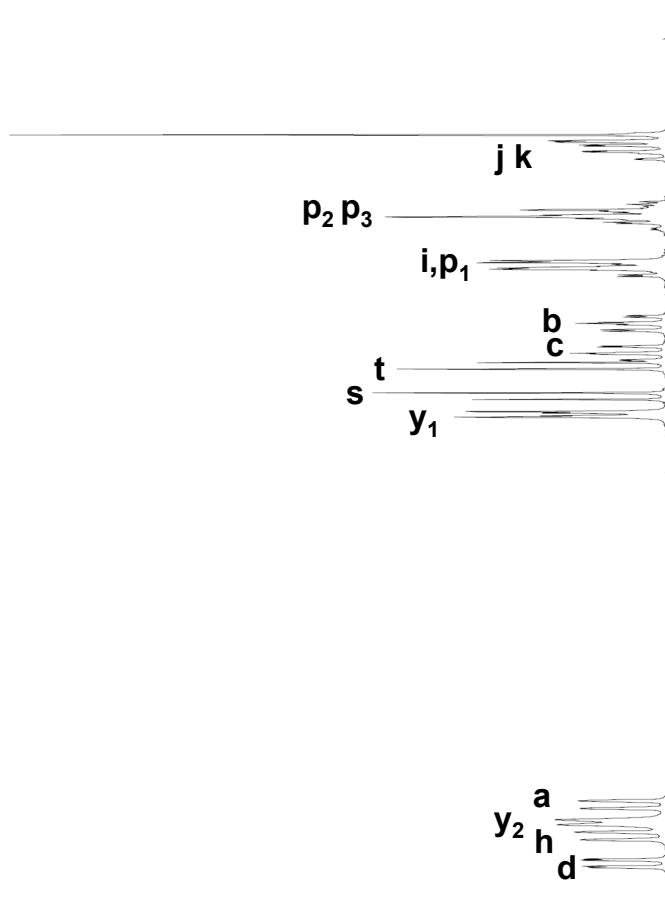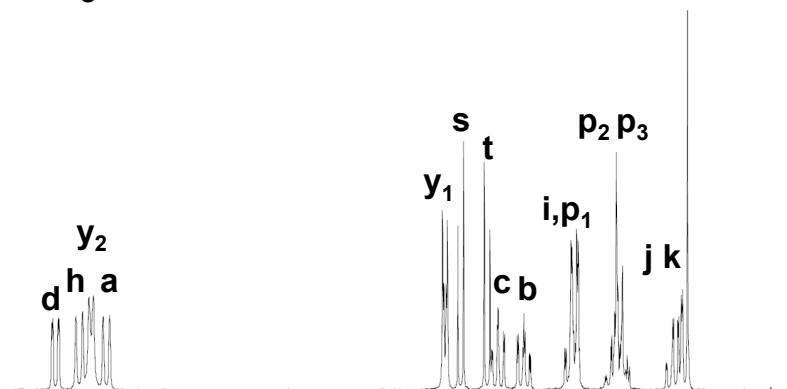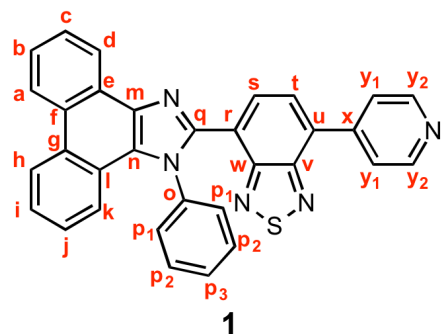| Acquisition Time (sec)	1.0912	D	0.00345	D1	2	DE	6	DS	4
Date	17 Oct 2018 10:47:49			Date Stamp	17 Oct 2018 10:47:49				
File Name	C:¥Users¥Asami-Lab¥Desktop¥10¥PDATA¥1¥1r			Frequency (MHz)	125.7578	GB	0	INSTRUM	\<spect\>
LB	1	NS	1024	Nucleus	13C	Number of Transients	1024	Origin	spect
Original Points Count	32768	Owner	root	PC	1.4	PROBHD	\<5 mm BBO BB-1H Z-GRD Z859001/0006 \>		
PULPROG	\<zgpg30\>	Points Count	32768	Pulse Sequence	zgpg30	Receiver Gain	4597.60	SF	125.757789
SFO1	125.770364304853			SI	32768	SSB	0	SW(cyclical) (Hz)	30030.03
SWH	30030.03003003			Solvent	CHLOROFORM-d			Spectrum Offset (Hz)	12572.4346
Spectrum Type	standard	Sweep Width (Hz)	30029.11	TD	65536	TD0	1	TE	299.5
Temperature (degree C)	26.500	WDW	1						

CDCl$_3$

S21

Partial ^{13}C NMR spectrum of **1** (500 MHz, in CDCl$_3$, rt)

Acquisition Time (sec)	1.0912	D		0.00345	D1	2	DE	6	DS	4
Date	17 Oct 2018 10:47:49				Date Stamp	17 Oct 2018 10:47:49				
File Name	C:¥Users¥Asami-Lab¥Desktop¥10¥PDATA¥1¥1r				Frequency (MHz)	125.7578	GB	0	INSTRUM	<spect>
LB	1	NS		1024	Nucleus	13C	Number of Transients	1024	Origin	spect
Original Points Count	32768	Owner		root	PC	1.4	PROBHD	<5 mm BBO BB-1H Z-GRD Z859001/0006 >		
PULPROG	<zgpg30>	Points Count		32768	Pulse Sequence	zgpg30	Receiver Gain	4597.60	SF	125.757789
SFO1	125.770364304853				SI	32768	SSB	0	SW(cyclical) (Hz)	30030.03
SWH	30030.03003003				Solvent	CHLOROFORM-d			Spectrum Offset (Hz)	12572.4346
Spectrum Type	standard	Sweep Width (Hz)		30029.11	TD	65536	TD0	1	TE	299.5
Temperature (degree C)	26.500	WDW		1						

1

p$_2$ p$_3$

p$_1$

g

f

n

t

c

e

j

b

i

r

h

y$_1$

a

d, l

k

129.56 129.59 129.64	128.92	128.42 128.26	127.77	127.38 127.18	126.36	125.84	125.33	125.00	124.17	123.57	123.14	122.85	121.07	

Chemical Shift (ppm)

S22
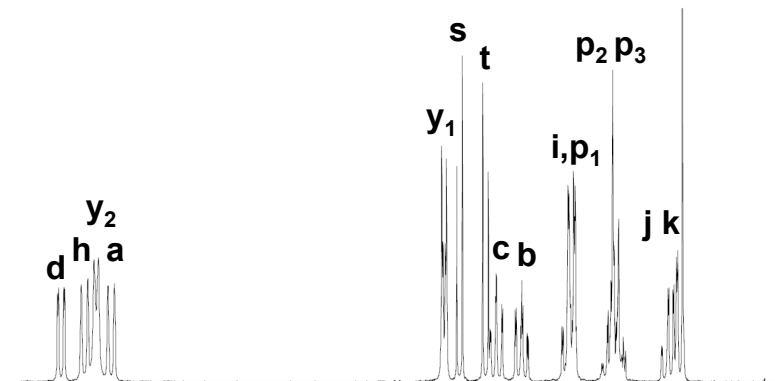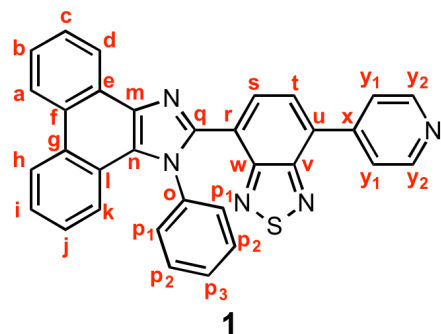
Partial ^{13}C NMR spectrum of **1** (500 MHz, in CDCl$_3$, rt)

| Acquisition Time (sec)	1.0912	D		0.00345	D1	2	DE	6	DS	4
Date	17 Oct 2018 10:47:49				Date Stamp	17 Oct 2018 10:47:49				
File Name	C:¥Users¥Asami-Lab¥Desktop¥10¥PDATA¥1¥1r				Frequency (MHz)	125.7578	GB	0	INSTRUM	<spect>
LB	1	NS		1024	Nucleus	13C	Number of Transients	1024	Origin	spect
Original Points Count	32768	Owner		root	PC	1.4	PROBHD	<5 mm BBO BB-1H Z-GRD Z859001/0006 >		
PULPROG	<zgpg30>	Points Count		32768	Pulse Sequence	zgpg30	Receiver Gain	4597.60	SF	125.757789
SFO1	125.770364304853				SI	32768	SSB	0	SW(cyclical) (Hz)	30030.03
SWH	30030.03003003				Solvent	CHLOROFORM-d			Spectrum Offset (Hz)	12572.4346
Spectrum Type	standard	Sweep Width (Hz)		30029.11	TD	65536	TD0	1	TE	299.5
Temperature (degree C)	26.500	WDW		1						

S23

Partial COSY spectrum of **1** (500 MHz, in CDCl₃, rt)

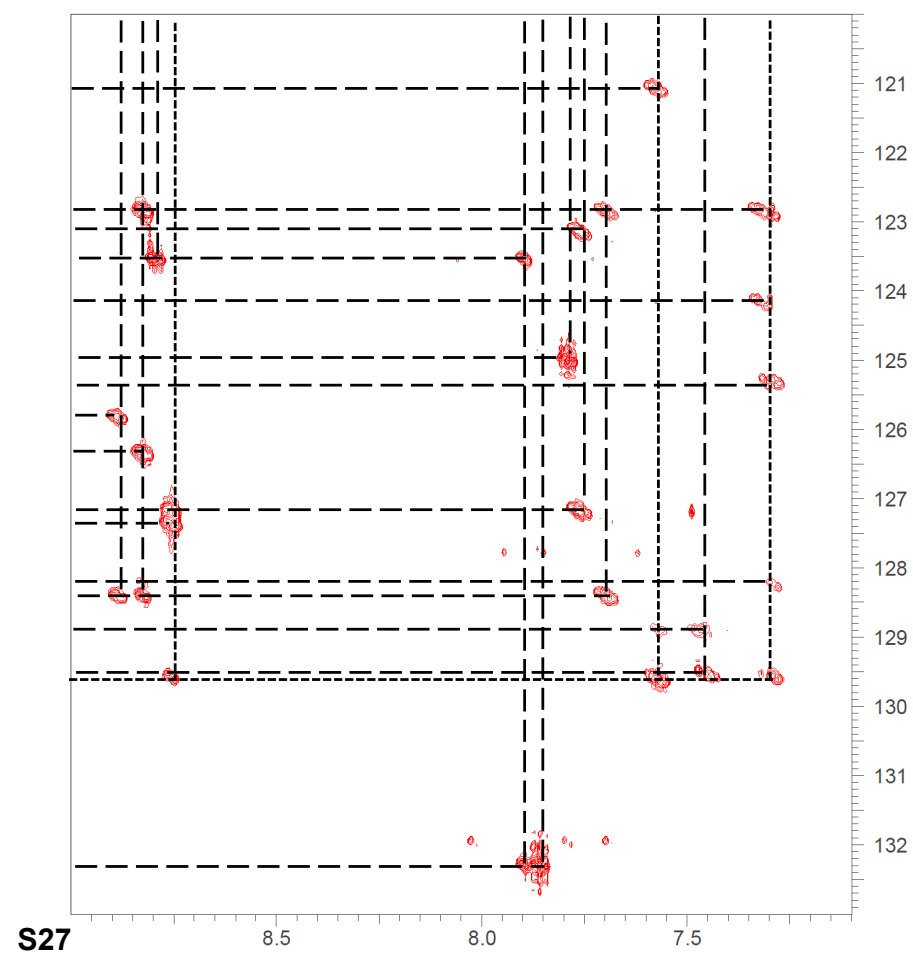Partial HSQC spectrum of **1** (500 MHz, in CDCl$_3$, rt)
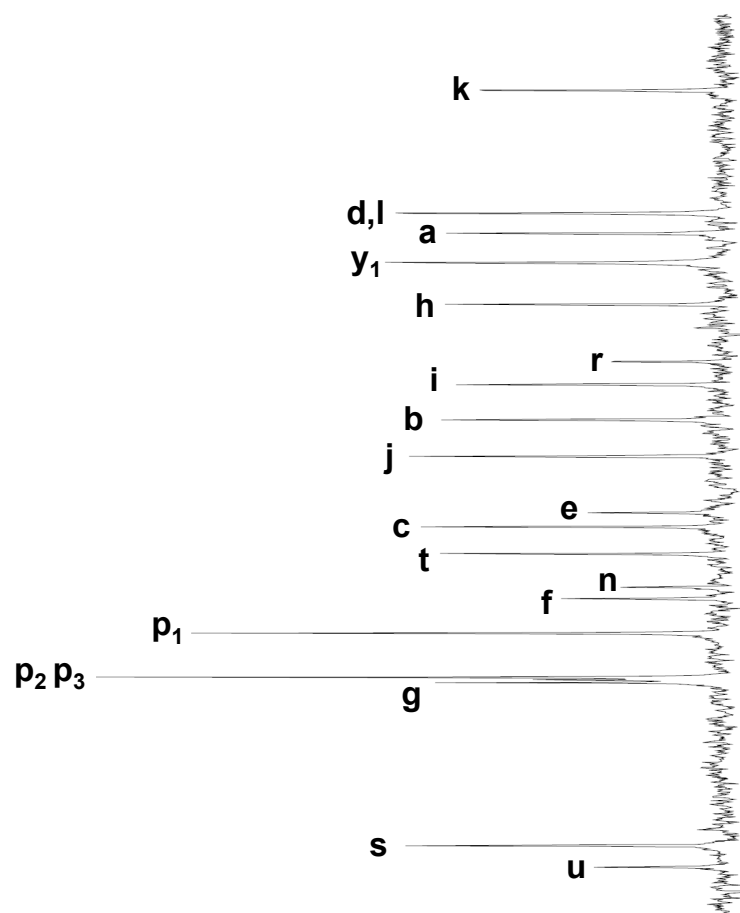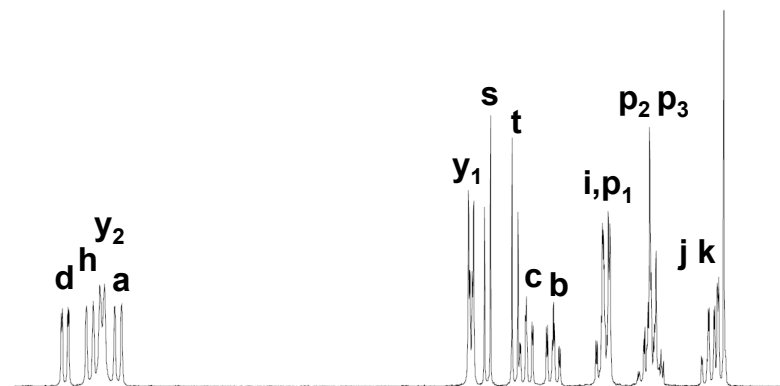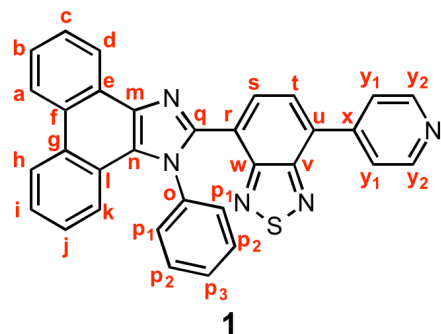
S25

Partial HSQC spectrum of **1** (500 MHz, in CDCl$_3$, rt)

S26
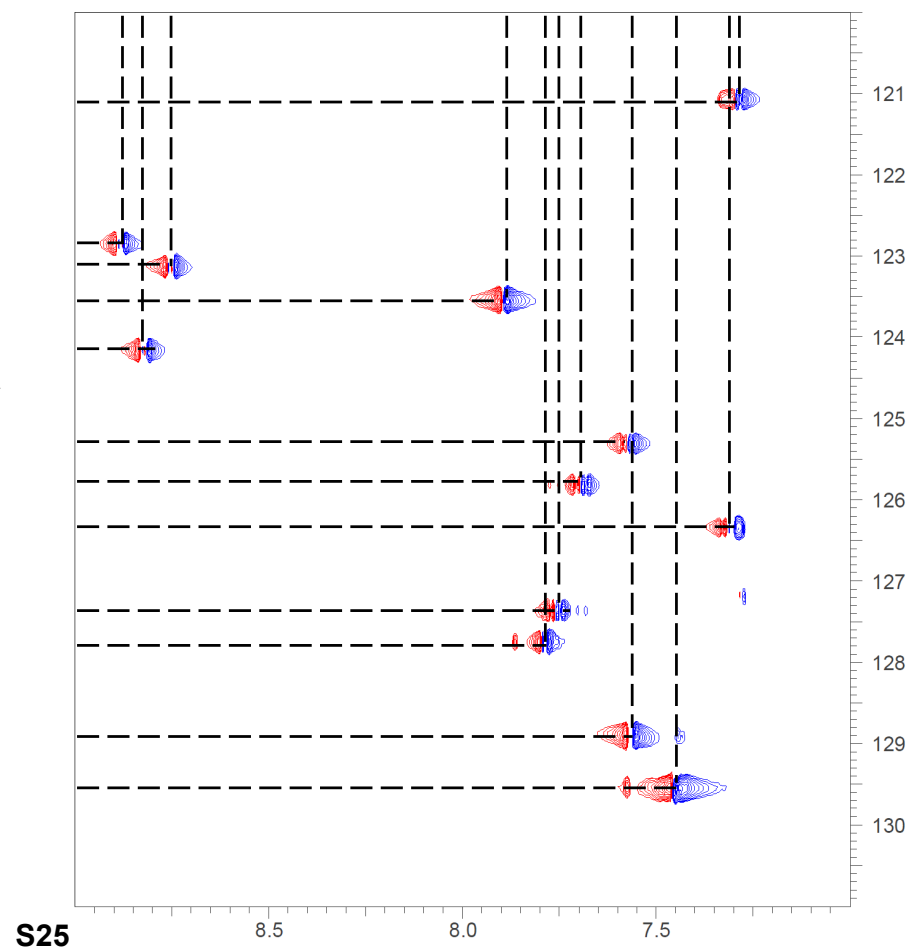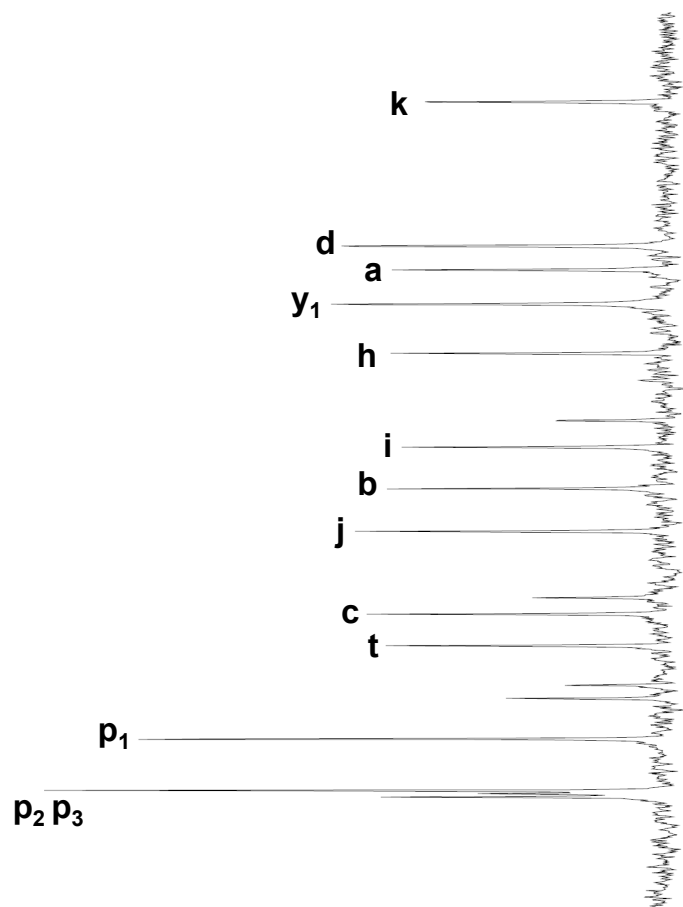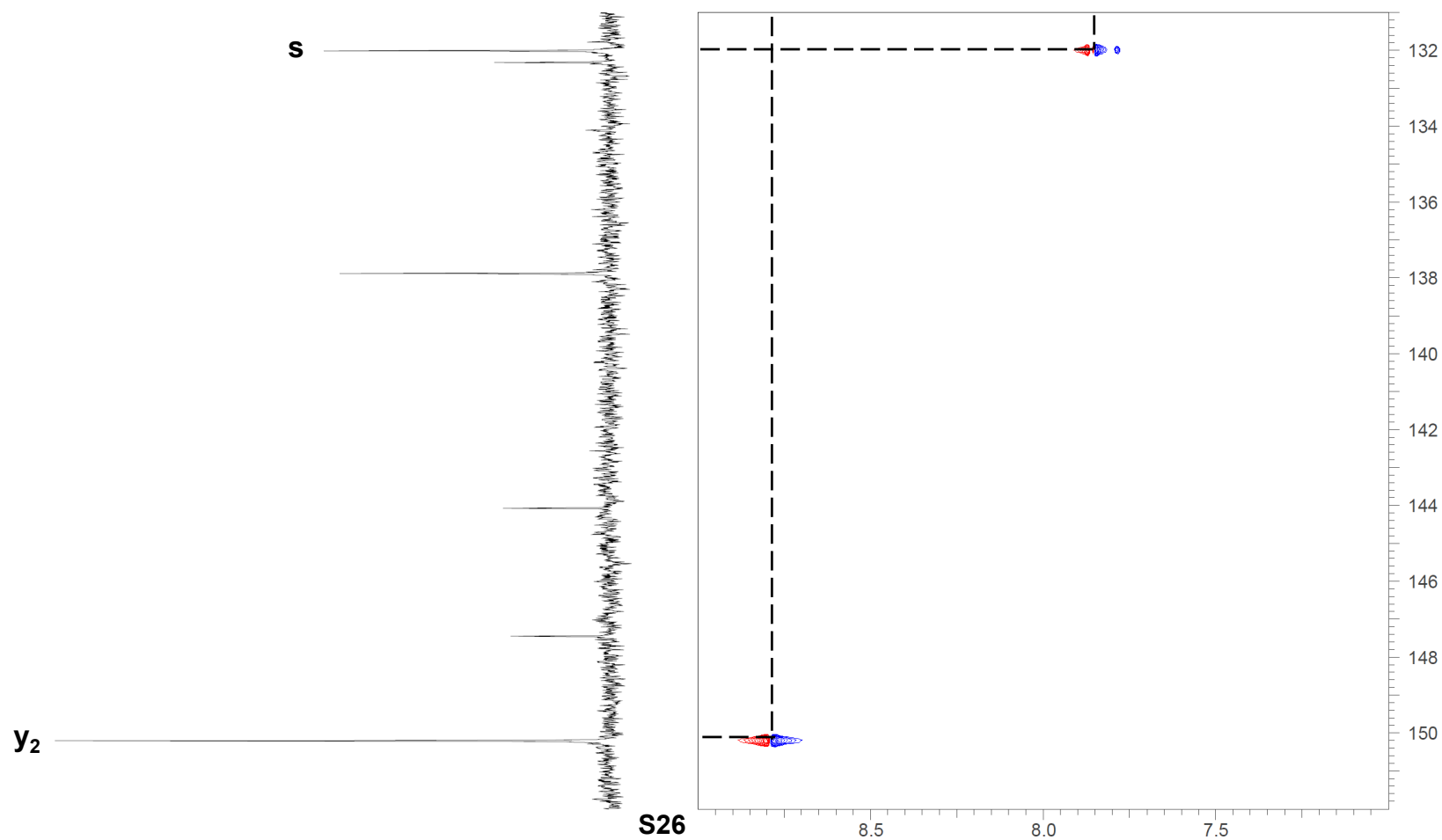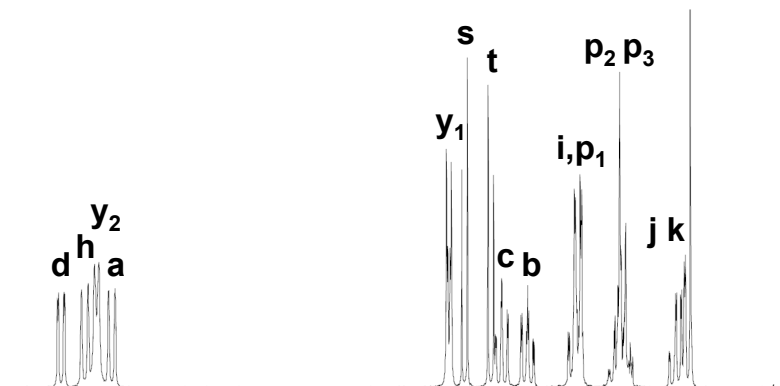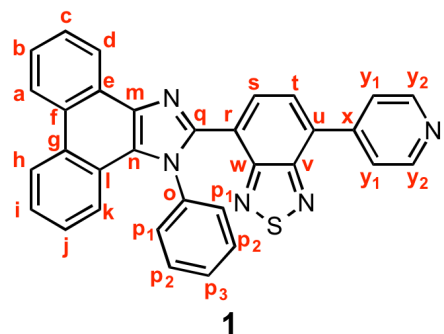
Partial HMBC spectrum of **1** (500 MHz, in CDCl₃, rt)

Partial HMBC spectrum of **1** (500 MHz, in CDCl$_3$, rt)