Electronic Supplementary Information

Photoreversible negative photochromism in N-(3,5-dichlorosalicylidene)-1-aminopyrene

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General procedures

The NMR spectrum in $CDCl_3$ was obtained on a Bruker AC 300 MHz spectrometer at 25 °C. Chemical shifts are reported with reference to $SiMe_4$. Elemental analysis was performed on a Perkin Elmer 2400 CHN microanalyser. Diffuse reflectance spectra were obtained with a Varian Cary 5E spectrometer using polytetrafluoroethylene (PTFE) as a reference. The solid-state emission spectrum was obtained with a Fluorolog-3 (Jobin-Yvon-Spex Company) spectrometer. Kubelka Munk and emission spectra were normalized to allow meaningful comparisons. Light irradiations were carried out with a LOT-ORIEL 200 W high-pressure mercury Arc lamp (LSN261) equipped with suitable filters.

Synthesis of N-(3,5-dichlorosalicylidene)-1-aminopyrene (1)

A solution of 1-aminopyrene (0.5 mmol, 0.109 g) dissolved in ethanol (20 mL) was added to a solution of 3,5-dichlorosalicylaldehyde (0.55 mmol, 0.105 g) in the same solvent (10 mL). The resulting dark red solution was stirred for 30 min and, afterwards, heated at reflux for 2 h. It was then allowed to cool to room temperature to give red plates, which were filtered, washed with ethanol (10 mL) and n-hexane (3 × 50 mL), and dried under vacuum.

Yield: 0.168 g (86%). ^{1}H NMR: δ = 7.39 (d, $^4J_{H,H}$ = 2.6 Hz, 1H, 4-H, C_6H_2), 7.52 (d, $^4J_{H,H}$ = 2.6 Hz, 1H, 6-H, C_6H_2), 7.82 (d, $^3J_{H,H}$ = 8.6 Hz, 1H, pyrene), 8.01–8.10 (m, 3H, pyrene), 8.13–8.26 (m, 4H, pyrene), 8.49 (d, $^3J_{H,H}$ = 8.6 Hz, 1H, pyrene), 8.79 (s, 1H, CHN), 14.67 (s, 1H, OH) ppm. *Anal*. Calc. for $C_{23}H_{13}Cl_2NO$ (390.27): C 70.79, H 3.36, N 3.59. Found: C 70.93, H 3.42, N 3.66.

X-Ray crystallography

The X-ray data for **1** were collected at 173(2) K on a STOE IPDS-II diffractometer with graphite-monochromatised Mo-K_α radiation generated by a fine-focus X-ray tube operated at 50 kV and 40 mA. The reflections of the images were indexed, integrated and scaled using the X-Area data reduction package.[1] Data were corrected for absorption using the PLATON program.[2] The structures were solved by direct methods

using the SHELXS-97 program[3] and refined first isotropically and then anisotropically using SHELXL-97.[3] Hydrogen atoms were revealed from $\Delta\rho$ maps and those bonded to C were refined using appropriate riding models. Figures were generated using the program Mercury.[4]

$C_{23}H_{13}Cl_2NO$, $M_r = 355.80$ g mol^{-1}, triclinic, space group P–1, $a = 7.8740(13)$, $b = 8.3670(14)$, $c = 13.195(2)$ Å, $\alpha = 91.615(14)$, $\beta = 103.438(13)$, $\gamma = 90.080(14)°$, $V = 845.1(2)$ Å^3, $Z = 2$, $\rho = 1.534$ g cm^{-3}, μ(Mo-Kα) = 0.398 mm^{-1}, reflections: 8702 collected, 3157 unique, $R_{int} = 0.0948$, R_1(all) = 0.0613, wR_2(all) = 0.1249.

CCDC 978838 contains the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

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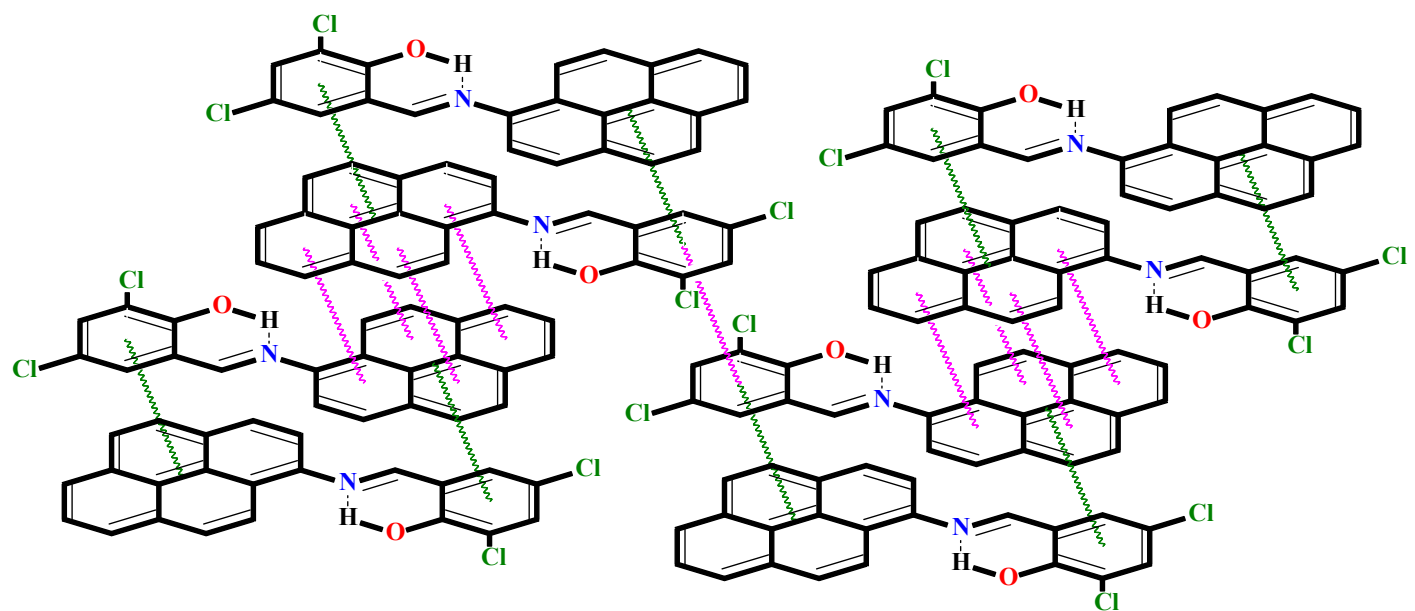
Chart S1 Simplified line diagram of $\pi\cdots\pi$ stacking interactions in the crystal structure of **1**. The head-to-head and head-to-tail interactions are shown in pink and green, respectively.

Table S3 Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths

Cl(1)–C(23)	1.729(2)	C(5)–C(6)	1.433(3)	C(13)–C(14)	1.400(3)
Cl(2)–C(25)	1.740(2)	C(6)–C(7)	1.400(3)	C(13)–C(17)	1.432(3)
O(1)–C(22)	1.337(3)	C(6)–C(16)	1.423(3)	C(14)–C(15)	1.375(3)
N(1)–C(1)	1.284(3)	C(7)–C(8)	1.389(4)	C(16)–C(17)	1.427(3)
N(1)–C(2)	1.412(3)	C(8)–C(9)	1.381(3)	C(21)–C(22)	1.417(3)
C(1)–C(21)	1.454(3)	C(9)–C(10)	1.403(3)	C(21)–C(26)	1.403(3)
C(2)–C(3)	1.412(3)	C(10)–C(11)	1.439(3)	C(22)–C(23)	1.393(3)
C(2)–C(15)	1.403(3)	C(10)–C(16)	1.416(3)	C(23)–C(24)	1.381(3)
C(3)–C(4)	1.434(3)	C(11)–C(12)	1.355(3)	C(24)–C(25)	1.392(3)
C(3)–C(17)	1.417(3)	C(12)–C(13)	1.423(3)	C(25)–C(26)	1.369(3)
C(4)–C(5)	1.353(3)				

Bond angles

C(1)–N(1)–C(2)	121.82(18)	C(6)–C(16)–C(17)	119.5(2)	C(14)–C(15)–C(2)	120.8(2)
N(1)–C(1)–C(21)	120.99(19)	C(7)–C(6)–C(5)	123.0(2)	C(15)–C(2)–C(3)	119.7(2)
C(3)–C(2)–N(1)	117.38(17)	C(7)–C(6)–C(16)	118.8(2)	C(15)–C(14)–C(13)	121.81(18)
C(15)–C(2)–N(1)	122.71(19)	C(8)–C(7)–C(6)	120.9(2)	C(16)–C(6)–C(5)	118.3(2)
O(1)–C(22)–C(23)	120.18(19)	C(8)–C(9)–C(10)	120.9(2)	C(16)–C(10)–C(11)	119.2(2)
O(1)–C(22)–C(21)	121.7(2)	C(9)–C(8)–C(7)	120.4(2)	C(16)–C(17)–C(13)	118.9(2)
C(22)–C(23)–Cl(1)	119.26(17)	C(9)–C(10)–C(11)	121.9(2)	C(17)–C(3)–C(4)	118.3(2)
C(24)–C(23)–Cl(1)	118.63(17)	C(9)–C(10)–C(16)	119.0(2)	C(22)–C(21)–C(1)	120.8(2)
C(24)–C(25)–Cl(2)	118.75(18)	C(10)–C(16)–C(6)	120.0(2)	C(23)–C(22)–C(21)	118.1(2)
C(26)–C(25)–Cl(2)	120.15(17)	C(10)–C(16)–C(17)	120.51(18)	C(23)–C(24)–C(25)	118.9(2)
C(2)–C(3)–C(4)	122.5(2)	C(11)–C(12)–C(13)	122.30(19)	C(24)–C(23)–C(22)	122.09(19)
C(2)–C(3)–C(17)	119.17(18)	C(12)–C(11)–C(10)	120.2(2)	C(25)–C(26)–C(21)	120.25(19)
C(3)–C(17)–C(13)	120.5(2)	C(12)–C(13)–C(17)	119.0(2)	C(26)–C(21)–C(1)	119.59(19)
C(3)–C(17)–C(16)	120.65(18)	C(14)–C(13)–C(12)	123.06(18)	C(26)–C(21)–C(22)	119.6(2)
C(4)–C(5)–C(6)	122.05(19)	C(14)–C(13)–C(17)	118.0(2)	C(26)–C(25)–C(24)	121.1(2)
C(5)–C(4)–C(3)	121.0(2)				

Torsion angles

C(1)–N(1)–C(2)–C(3)	160.6(2)	C(1)–N(1)–C(2)–C(15)	–24.6(3)

Table S2. Hydrogen bond lengths (Å) and angles (°) for **1**

D–H⋯A	d(D–H)	d(H⋯A)	d(D⋯A)	∠(DHA)
O(1A)–H(1OA)⋯N(1A)	0.84(4)	1.77(3)	2.577(2)	159(3)

Table S3. π···π bond lengths (Å) and angles (°) for **1**[a]

Cg(I)	Cg(J)	d[Cg(I)–Cg(J)]	α	β
Cg(1)	Cg(1)#1	4.3405(16)	0.00	36.87
Cg(1)	Cg(1)#2	4.6370(16)	0.00	43.97
Cg(1)	Cg(2)#1	3.8427(16)	3.38	23.93
Cg(1)	Cg(2)#2	4.8675(17)	3.38	47.36
Cg(1)	Cg(3)#1	3.7798(15)	3.98	26.18
Cg(1)	Cg(4)#1	3.5778(15)	2.65	17.54
Cg(2)	Cg(1)#1	3.8428(16)	3.38	27.17
Cg(2)	Cg(1)#2	4.8674(17)	3.38	49.19
Cg(2)	Cg(2)#1	4.7646(16)	0.00	44.69
Cg(2)	Cg(4)#1	3.8347(15)	2.57	26.52
Cg(3)	Cg(1)#1	3.7799(15)	3.98	24.8
Cg(3)	Cg(5)#2	4.4971(16)	30.26	27.89
Cg(4)	Cg(1)#1	3.5778(15)	2.65	17.03
Cg(4)	Cg(2)#1	3.8347(15)	2.57	24.2
Cg(4)	Cg(4)#1	4.3353(15)	0.00	36.8
Cg(4)	Cg(5)#2	4.0737(15)	28.87	14.3
Cg(5)	Cg(3)#2	4.4971(16)	30.26	57.7
Cg(5)	Cg(4)#2	4.0737(15)	28.87	33.6
Cg(5)	Cg(5)#1	3.8615(15)	0.00	27.48

[a] Cg(I)–Cg(J): distance between ring centroids; α: dihedral angle between planes Cg(I) and Cg(J); β: angle Cg(I) → Cg(J) vector and normal to plane I. Symmetry transformations used to generate equivalent atoms: #1 1 − x, −y, 1 − z; #2 1 − x, 1 − y, 1 − z; Cg(1): C(2)–C(3)–C(17)–C(13)–C(14)–C(15), Cg(2): C(3)–C(4)–C(5)–C(6)–C(16)–C(17), Cg(3): C(6)–C(7)–C(8)–C(9)–C(10)–C(16), Cg(4): C(10)–C(11)–C(12)–C(13)–C(17)–C(16), Cg(5): C(21)–C(22)–C(23)–C(24)–C(25)–C(26).