

A novel chromogenic host compound that shows sensitive color change upon inclusion crystallization†

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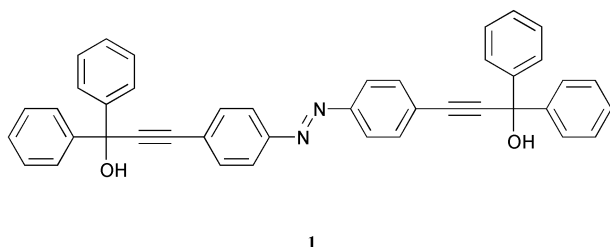
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A new azo group containing host compound, 3-{4-[4-(3-hydroxy-3,3-diphenylprop-1-ynyl)phenylazo]phenyl}-1,1-diphenylprop-2-yn-1-ol (1**), exhibits a color change from yellow to red upon inclusion complexation with various guest compounds in the solid state.**

The design of novel chromogenic host molecules that exhibit sensitive color changes upon complexation with guest molecules has attracted increasing attention because of their potential applications in analytical and material sciences.¹ However, only a few imidazole derivatives that exhibit color changes upon complexation of guest compounds are known.² Here, we report a novel chromogenic host compound **1**, which shows a marked color change upon inclusion complex formation. The yellow host compound **1** gave an inclusion complex of orange to red color upon recrystallization from the guest solvent. The color change was also found when **1** was exposed to the guest vapor in the solid state.







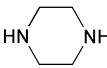
The host compound **1** was prepared by a Pd(II) catalyzed coupling reaction of 4,4'-dibromoazobenzene³ with 1,1-diphenylprop-2-yn-1-ol as yellow prisms in 68% yield. The host **1** formed stable inclusion complexes with various guest compounds, and the color of the crystals changed from yellow (guest-free) to orange or red upon complexation (Table 1). The solid-state UV spectra of **1** and its 1 : 2 inclusion complex with DMF are shown in Fig. 1. The red-shift of the spectrum of the inclusion complex was also observed for all the compounds specified in Table 1, and this can be attributed to intermolecular host–host charge-transfer interactions.

Interestingly, when the guest-free crystals of **1** were placed in a vessel saturated with guest vapor at room temperature, the color of the crystals turned from yellow to red or orange. For example, when exposed to pyridine vapor at room temperature for 4 h, the yellow crystals of **1** changed into the 1 : 3 inclusion crystals of red color. Similarly, **1** formed 1 : 2 inclusion crystals with DMF and DMSO under gas–solid reaction conditions

after exposure for 24 and 72 h to the respective solvent vapours. Upon heating in the solid-state, these inclusion complex crystals lost their guests to give free host crystals of yellow color.

To investigate the relationship between the color of the crystals and the molecular packing in the crystals, the crystal structures of the guest-free **1** and the 1 : 2 inclusion complex of **1** with DMF were determined by X-ray analysis. Compound **1** crystallizes in the space group $P\bar{1}$ with one-half host molecule in the asymmetric unit, the remainder of the molecule being generated by an inversion center. One of the terminal phenyl rings is coplanar with that of the host 'backbone' [dihedral angle = 2.73(6)°] while the other is twisted approximately perpendicular [dihedral angle = 89.03(5)°] to this, as illustrated in Fig. 2. Each hydroxy group is hydrogen-bonded to the N atom of an adjacent host such that a flat hydrogen-bonded ribbon with protruding phenyl rings is formed. The distance between offset hydrogen-bonded molecular backbones is *ca.* 3.6 Å. These flat ribbons propagate along the [110] direction and pack side-by-side with interdigitated phenyl rings with the ribbons above and below as shown in Fig. 2.

Table 1 Host-guest ratio and color of the inclusion complex with **1**

Guest	H : G	Color
Me ₂ NCHO	1 : 2	Red
PhN(Me)CHO	1 : 2	Red
	1 : 2	Red
	1 : 2	Red
Me ₂ S=O	1 : 2	Orange
	1 : 3	Red
	1 : 2	Orange
	1 : 1	Orange
Me ₂ NCH ₂ NMe ₂	1 : 2	Red
Me ₂ N-(CH ₂) ₂ -NMe ₂	1 : 2	Orange-red
Me ₂ N-(CH ₂) ₃ -NMe ₂	1 : 2	Orange-red

† Electronic supplementary information (ESI) available: molecular structures of **1** and **1**·2DMF. See <http://www.rsc.org/suppdata/nj/b1/b111359c/>

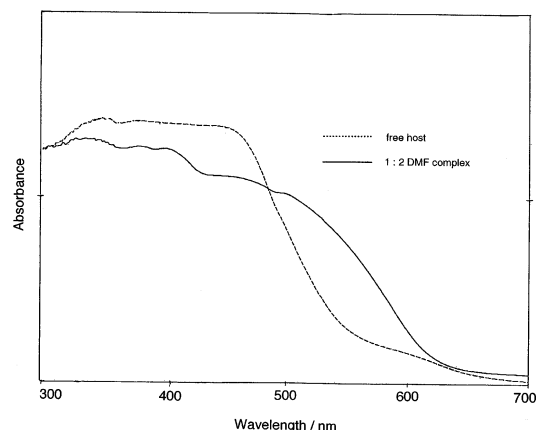


Fig. 1 Solid-state UV spectra of **1** and its 1 : 2 DMF complex.

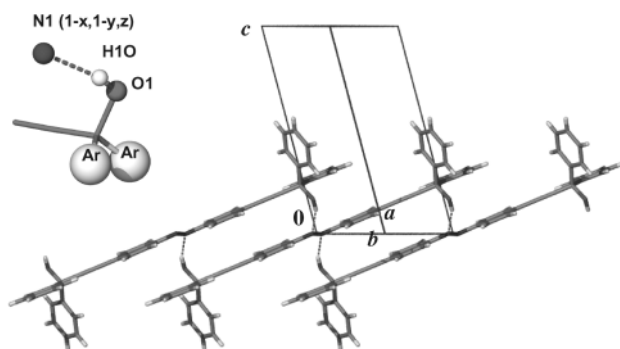


Fig. 2 Crystal packing of **1** viewed down [110] showing co-planarity of one terminal phenyl ring and the 'backbone,' as well as O–H...N hydrogen bonds, illustrated in the inset. Hydrogen bond geometry: O–H = 0.94 Å, O...N = 3.019(2) Å, H...N = 2.11 Å, O–H...N = 162°.

The 1 : 2 DMF inclusion complex exhibits crystal packing quite different to that of **1** alone. The inclusion complex also crystallizes in the space group $P\bar{1}$ but the asymmetric unit consists of two independent half host molecules and hydrogen-bonded guest DMF molecules. The remainder of each of the host molecules is, again, generated by an inversion center and the conformation of each is similar but not identical. Unlike **1** alone, neither of the terminal phenyl rings are co-planar with the 'backbone' [dihedral angles are 72.87(5)°, 65.88(7)°, 59.48(7)° and 76.22(5)°] nor are any O–H...N hydrogen bonds noted. Instead, each host hydroxy group is hydrogen-bonded to the carbonyl oxygen of the DMF guest molecules. The host molecules are crossed, as illustrated in Fig. 3, and form columns of stacked hosts with the rod-like backbones at *ca.* 45° with respect to each other.

Apart from the hydrogen bonding interactions, both crystals are further stabilized by distinct C–H... π interactions reminiscent of the fourfold 'phenyl embraces' described by Scudler and Dance.⁴ The host **1** alone exhibits a single concerted interaction, as illustrated in Fig. 4(a), while the inclusion complex **1**:2DMF exhibits one such set of interactions and one 'frustrated' embrace where the methyl group of a DMF guest molecule interrupts the phenyl–phenyl edge-to-face interaction [Fig. 4(b)].

The color changes noted upon guest complexation arise due to the distinctly different conformations adopted by host **1** in the absence and presence of guest molecules. Hydrogen bonding of host OH groups to guest acceptors allows the terminal phenyl rings to twist out of the plane of the conjugated system of the backbone and destroys the OH...N hydrogen bond, altering the energy associated with charge

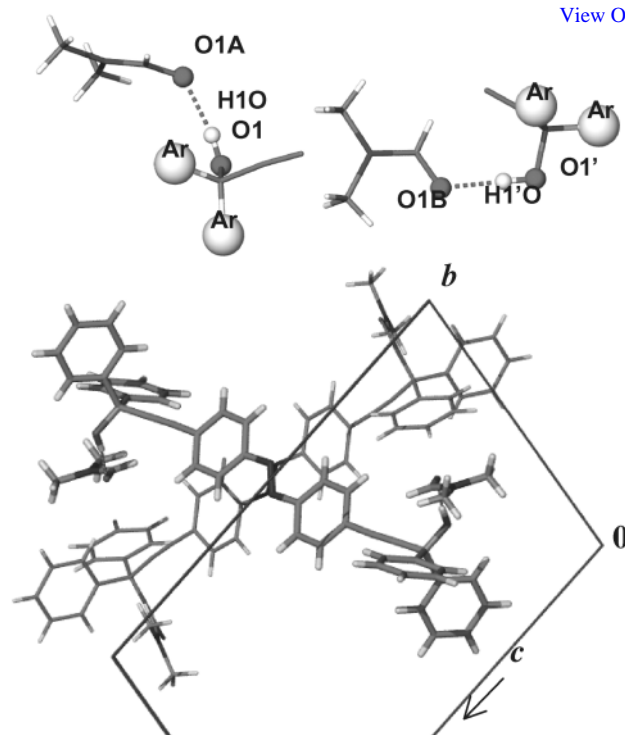


Fig. 3 Two crystallographically independent molecules viewed down [100] showing the 'crossed' packing of the backbones of **1** and hydrogen-bonded DMF guest molecules. O...O hydrogen bonds between host and guest are illustrated in the inset. Hydrogen bond geometry: O1–H1O...O1A, O–H = 0.90(3), O...O = 2.749(4), H...O = 1.86(3) Å, O–H...O = 170(2)°, O1'–H1'O...O1B ($x-1, y+1, z$), O–H = 0.91(3), O...O = 2.700(2), H...O = 1.79(3) Å, O–H...O = 179(2)°.

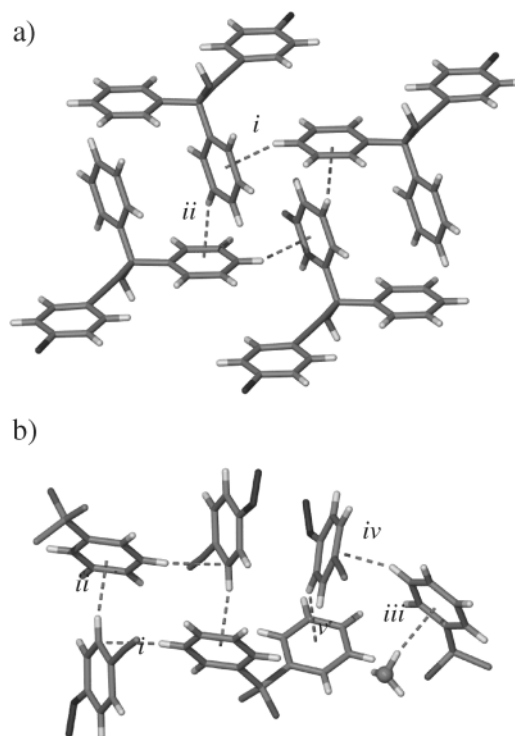


Fig. 4 Fourfold 'phenyl embrace' type interactions in (a) host **1** alone (1/2 host shown): *i* H...centroid = 2.83 Å, C–H...centroid = 154°; *ii* H...centroid = 2.78 Å, C–H...centroid = 145° and (b) **1**:2DMF complex (relevant phenyl rings and guest molecule methyl group shown): *i* H...C = 2.84 Å, C–H...centroid = 143°; *ii* H...centroid = 2.83 Å, C–H...centroid = 145°; *iii* H...centroid = 2.70 Å, C–H...centroid = 147°; *iv* H...centroid = 2.68 Å, C–H...centroid = 153°; *v* H...centroid = 3.02 Å, C–H...centroid = 157°.

transfer interactions between the unsaturated systems and thus affecting the color.

Experimental

Synthesis of **1**

4,4'-Dibromoazobenzene (2.0 g, 5.9 mmol), 1,1-diphenylprop-2-yn-1-ol (2.5 g, 11.8 mmol), PdCl₂(PPh₃)₂ (0.05 g), PPh₃ (0.05 g) and Et₃N (100 ml) were mixed and heated under reflux for 4 h. After filtration of Et₃N·HBr, the Et₃N solution was evaporated to leave crude **1**. Recrystallization from toluene gave pure **1** as yellow prisms (2.13 g, 68% yield). Mp 224–227 °C; IR (Nujol) 3412 cm⁻¹; UV (CHCl₃) λ_{max}/nm (ε) 243 (19 400), 364 (45 300); ¹H NMR (300 MHz, CDCl₃) δ 7.30–7.92 (m, 28 H), 2.89 (s, 2 H). Anal. calcd For C₄₂H₃₀N₂O₂: C, 84.82; H, 5.08; N, 4.71. Found: C, 84.72; H, 5.24; N, 4.41.

X-Ray structures

Data were collected on an Enraf–Nonius Kappa CCD diffractometer at 123 K using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, 1° φ and ω scans). Structures were solved by direct methods using the program SHELXS-97⁵ and refined by full-matrix least-squares refinement on F² using the programs SHELXL-97⁶ and X-Seed.⁷ The molecular diagrams of **1** and **1**·2 DMF are shown in the ESI.

Crystal data for **1**

C₄₂H₃₀N₂O₂, M_r = 596.68, triclinic, space group P $\bar{1}$, *a* = 6.7388(2), *b* = 8.7259(3), *c* = 14.5005(6) Å, α = 103.643(1), β = 94.729(2), γ = 106.122(2)°, *U* = 785.96(5) Å³, *Z* = 1, *D*_{calc} = 1.256 g cm⁻³, μ(Mo-Kα) = 0.077 mm⁻¹. Of 7755 reflections measured, 3796 were unique (*R*_{int} = 0.043) with 2293 *I* > 2σ(*I*), *R* indices [*I* > 2σ(*I*)] *R*₁ = 0.0576, *wR*₂ = 0.1215, GoF on *F*² = 0.995 for 209 refined parameters and 0 restraints.

Crystal data for **1**·2DMF

C₄₈H₄₄N₄O₄ (two 1/2 hosts + two guests), M_r = 740.87, triclinic, space group P $\bar{1}$, *a* = 8.8345(1), *b* = 12.1223(1), *c* = 19.1156(1) Å, α = 102.698(1)°, β = 93.471(1)°, γ = 97.473(1)°, *u* = 1971.72(3) Å³, *Z* = 2, *D*_{calc} = 1.248 g cm⁻³, μ(Mo-Kα) = 0.080 mm⁻¹. Of 19 898 reflections measured, 9498 were unique (*R*_{int} = 0.045) with 6076 *I* > 2σ(*I*), *R* indices [*I* > 2σ(*I*)] *R*₁ = 0.0584, *wR*₂ = 0.1241, GoF on *F*² = 1.026 for 520 refined parameters and 0 restraints. One of the DMF guest molecules exhibits disorder of the carbonyl group. Three positions are modeled for the guest carbonyl oxygen atom: two minor positions (20% site occupancy) and a primary position (60% site occupancy).

CCDC reference numbers 174130 and 174131. See <http://www.rsc.org/suppdata/nj/b1/b111359c/> for crystallographic data in CIF or other electronic format.

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