**SHORT PAPER**

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# Guest-selective colour and fluorescence changes of a novel fluorenone-based host compound[†]

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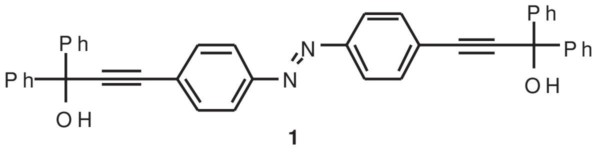
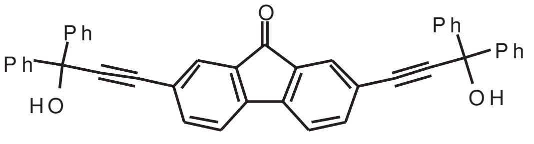
A new host compound, 2,7-bis-(3-hydroxy-3,3-diphenyl-prop-1-ynyl)-fluoren-9-one **(2)**, shows guest-selective colour change and fluorescence enhancement upon inclusion complexation in the solid state.

**Keywords:** colour change, fluorescence enhancement, fluorenone

Chromogenic host compounds have attracted much attention because they can be applied to sensor materials depending on their colour changes by host–guest complexation. However, only a few imidazole derivatives which show colour change upon complexation of guest compounds have been reported.[1] Recently, we have developed a series of new chromogenic host compounds, including 3-{4-[4-(3-hydroxy-3,3-diphenyl-prop-1-ynyl)-phenylazo]-phenyl}-1,1-diphenyl-prop-2-yn-1-ol (**1**), which show dramatic colour changes on inclusion complexation with various guest molecules in the solid state and in solution.[2] We now report a novel chromogenic host compound (**2**), which shows colour and fluorescence changes in the solid state upon inclusion complexation with specific guest compounds.



**1**



**2**

The host compound (**2**) was prepared by a Pd(II)-catalysed coupling reaction of 2,7-dibromofluoren-9-one with 1,1-diphenyl-prop-2-yn-1-ol as orange-yellow prisms in 38% yield. The host (**2**) gave inclusion compounds with ethyl formate (1:1), ethyl acetate (1:1), *n*-propyl acetate (2:1), *n*-butyl acetate(2:1), ethyl propionate (1:1), *n*-propyl propionate (2:1), THF (1:1), dioxane (1:2), toluene (2:1), DMF (1:1), DMSO (1:2), and pyridine (1:2), respectively. (Table 1). The orange–yellow crystals of **2**, upon complexation with ethyl formate and ethyl acetate, exhibited colour change to orange, whereas **2** yielded light yellow crystals by complexation with pyridine. A red-shift of the spectrum of the inclusion complex with ethyl acetate and a blue-shift of that with pyridine were observed in the solid state UV-spectra. (Fig. 1) The inclusion complexes with *n*-propyl acetate, *n*-butyl acetate, ethyl propionate, *n*-propyl propionate, THF, dioxane, toluene, DMF and DMSO showed the same orange–yellow colour as **2** itself. The colour change is highly guest-selective. The host molecule (**2**) recognizes the small difference between ethyl acetate and n-propyl acetate and exhibited the marked color change.

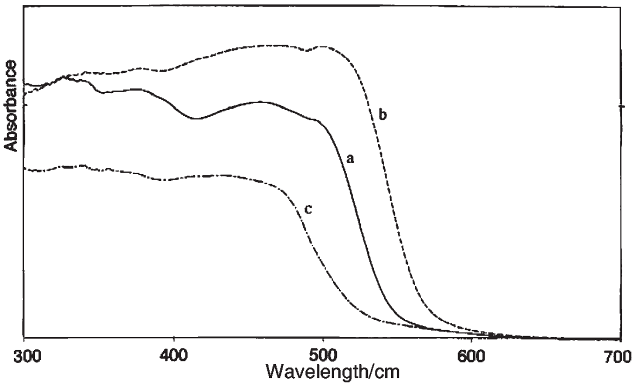


**Fig. 1** Solid-state UV spectra of guest-free host crystals (a), 1:1 ethyl acetate complex (b) and 1:2 pyridine complex (c).

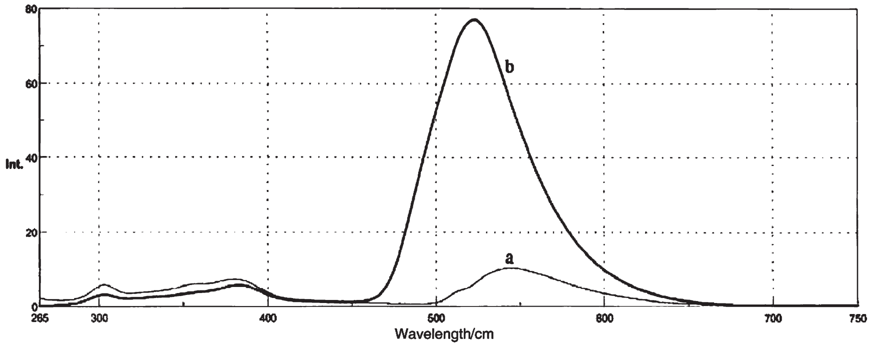


**Fig. 2** Fluorescence spectra of guest-free host crystals (a) and 1:2 pyridine complex (b).

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

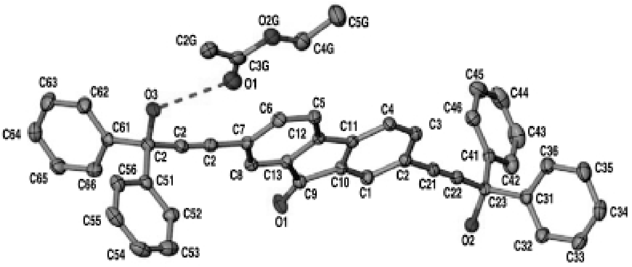

**Fig. 3** Molecular diagram of the asymmetric unit of the 1:1 ethyl acetate complex of **2**, indicating molecular numbering. Ellipsoids are presented at the 50% level and the host guest hydrogen bond depicted as a dotted line.

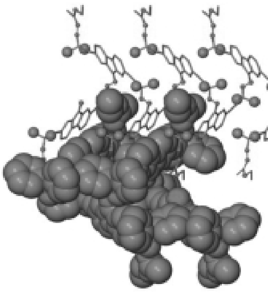

**Fig. 4** Packing diagram of the 1:1 ethyl acetate complex of **2**, viewed down *a*. A single bilayer is presented in stick mode with the terminal phenyl rings replaced by large spheres and oxygen atoms represented at 0.2 x van der Waals radius, while a second bilayer is depicted in spacefill mode. The interlayer digitation is clear with H-bonded ethyl acetate molecules penetrating into the neighbouring layer and all O─H···O bonds represented as dotted lines.

The solid-state fluorescence spectrum is also dramatically changed upon complexation with pyridine. The guest-free crystals of **2** exhibit weak fluorescence with emission maximum at 544 nm, whereas pyridine inclusion crystals exhibit 8-fold stronger fluorescence intensity with an emission maximum at 522 nm. (Fig. 2) This fluorescence emission is also highly guest-selective, and the inclusion crystals with other guest compounds did not show any fluorescence enhancement.

To investigate the molecular packing and host conformation in the solid-state, the crystal structure of the 1:1 inclusion complex of **2** with ethyl acetate was determined by X-ray analysis. *Crystal data* for **2**·ethyl acetate: $C_{47}H_{36}O_5$, $M_r$ = 680.76, monoclinic, space group $P2_1/c$, $a$ = 18.0679(2), $b$ = 8.3336(1), $c$ = 25.0952(5) Å, β = 108.960(1)°, $V$ = 3573.59(9) Å$^3$, $Z$ = 4, $D_{calc}$ = 1.265 g.cm$^{-3}$, μ(MoKα) = 0.081 mm$^{-1}$. 8660 Unique reflections, with 4260 $I>2\sigma(I)$, $R$ indices $[I>2\sigma(I)]$ $R_1$ = 0.0514, $wR_2$ = 0.1154, GoF on $F^2$ = 0.919 for 479 refined parameters and 2 restraints. CCDC 198545.

Host **2** with ethyl acetate guest crystallises in the space group $P2_1/c$ with one host molecule and one guest molecule in the asymmetric unit, as illustrated in Fig. 3. Terminal phenyl rings are twisted out of the plane of the central fluorenone moiety, which is typically planar (dihedral angles: 63.83(4), 72.72(6), 77.75(5) and 54.95(5)° for each terminal phenyl ring, in number order, relative to the fluorenone core). Host hydroxy groups form H-bonds with the guest molecule and with the carbonyl group of the fluorenone moiety of a neighbouring host yielding H-bonded bilayers with protruding guest molecules as illustrated in Fig. 4. H-bonding geometry: O2-H2O···O1 (-$x$+1, $y$+1/2, -$z$-1/2); O-H = 0.94(1) Å, O···O = 2.789(2) Å, H···O = 1.86(2) Å, ∠OHO = 171(2) ° and O3-H3O···O1G (-$x$+1, $y$-1/2, -$z$+1/2); O-H = 0.95(1) Å, O···O = 2.845(2) Å, H···O = 1.92(2) Å, ∠OHO = 164(2)°. These H-bonded bilayers interdigitate and a large number of weak interactions including C─H···π and C─H···O interactions stabilise the structure.

**Table 1** Host:guest (h:g) ratio and colour of inclusion complexes of **2**

| Guest | h:g[a] | Colour |
|---|---|---|
| Ethyl acetate | 1:1 | Orange |
| *n*-propyl acetate | 2:1 | Orange─yellow |
| *n*-butyl acetate | 2:1 | Orange─yellow |
| Ethyl propionate | 1:1 | Orange─yellow |
| *n*-propyl propionate | 2:1 | Orange─yellow |
| THF | 1:1 | Orange─yellow |
| Dioxane | 1:2 | Orange─yellow |
| Toluene | 2:1 | Orange─yellow |
| DMF | 1:1 | Orange─yellow |
| DMSO | 1:2 | Orange─yellow |
| Pyridine | 1:2 | Light yellow |

[a] Host-guest ratios were determined by $^1$H NMR and TG.

The νOH values of guest-free host crystals, 1:1 ethyl acetate complex and 1:2 pyridine complex are 3525 and 3406 cm$^{-1}$, 3384 cm$^{-1}$ and 3078 cm$^{-1}$, respectively. The relatively strong intermolecular hydrogen bond between the hydroxyl group of the host and the pyridine nitrogen atom is observed. These results suggest that the fluorescence enhancement be related to the host-host and host-guest packing in the crystals.

## Experimental

*Preparation* of **2**: 2,7-dibromofluoren-9-one (2.0 g, 5.9 mmol), 1, 1-diphenyl-prop-2-yn-1-ol (2.5 g, 11.8 mmol), $PdCl_2(PPh_3)_2$ (0.05 g), $PPh_3$ (0.05 g) and $Et_3N$ (150 ml) were mixed and heated under reflux for 6 h. After filtration of $Et_3N$· HBr, the $Et_3N$ solution was evaporated to leave crude **2**. Recrystallisation of this from MeOH gave pure **2** as orange-yellow prisms (1.32 g, 38% yield). M.p. 180─185 °C; IR (Nujol) 3523, 3428 (OH), 1706 (C=O) cm$^{-1}$; UV ($CHCl_3$) λmax/nm (ε) 287 (132000), 326 (27900), 339 (27800), 429 (2310); δH (300 MHz, $CDCl_3$) 7.29-7.81 (m, 26 H), 2.86 (s, 2 H). Anal. Calc. For $C_{43}H_{28}O_3$: C, 87.14; H, 4.76. Found: C, 87.14; H, 4.83.

*General procedure for the preparation of inclusion crystals*: Crystallisation of host compound (**2**) from a neat solution of various kinds of guest compounds at room temperature yielded inclusion complex crystals as shown in Table 1. The host─guest ratios were determined by $^1$H NMR and TG analyses.

Crystals suitable for single crystal x-ray diffraction experiments were grown by slow evaporation of a solution of the host in ethyl acetate. Data were collected on an Enraf-Nonius Kappa CCD diffratometer 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-97[3] and refined by full matrix least squares refinement on $F^2$ using the programs SHELXL-97[4] and XSeed.[5] Non-hydrogen atoms of both host and guest were refined anisotropically and hydrogen atoms inserted in geometrically determined positions with temperature factors fixed at 1.2 times (1.5 for methyl hydrogens) that of the parent atom.

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