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Guest-dependent novel photochromism of 7-bromo-1,4,8-triphenyl-2,3-benzo[3.3.0]octa-2,4,7-trien-6-one in its inclusion crystals

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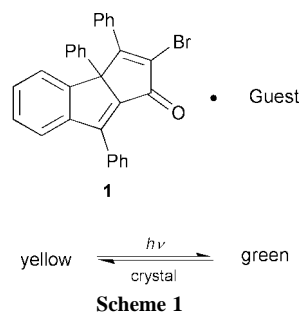
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Inclusion crystals of 7-bromo-1,4,8-triphenyl-2,3-benzo[3.3.0]octa-2,4,7-trien-6-one (**1**) showed a reversible color change from yellow to green on exposure to UV-light, and this depends on the guest molecules present.

Organic photochromic compounds have received considerable attention in recent years due to their potential applications such as information storage, electronic display systems, optical switching devices, ophthalmic glasses, and so on.¹ Several types of organic photochromic compounds such as naphthopyrans, spiropyrans, fulgides (dialkylidenesuccinic anhydrides), anils (*N*-phenyl imines), hydrazones, stilbenes, and diaryl-ethenes have been discovered and their properties investigated.² Recently, we have reported the novel photochromism of crystalline biindenylidene, which shows a reversible color change from yellow to reddish-purple upon photoirradiation.³ We have now found that the title compound **1** forms inclusion complex crystals with various kinds of organic guest molecules and some of these inclusion crystals show a reversible color change from yellow to green upon photoirradiation in the solid state (Scheme 1). It was also found that the stability of the photochromism depends on the type of guest molecule included. This is the first example of guest-dependent photochromism in host-guest inclusion crystals.

When a mixture of **1** and various kinds of guest compounds was recrystallized from AcOEt solution, inclusion complex crystals of **1** were obtained† (Table 1). Some of these inclusion crystals show a reversible color change from yellow to green upon photoirradiation in the solid state, although **1** itself does not show any photocoloration. For example, upon photoirradiation yellow crystals of the 2:1 inclusion compound of **1** with *p*-dimethoxybenzene turned green. These crystals revert to yellow on storage in the dark for 6 h at room temperature or quickly on heating at 60 °C. The UV spectral change of the 2:1 inclusion crystals is shown in Fig. 1. Similarly, the inclusion crystals with acetone (1:1), butan-2-one (1:1), cyclopentanone (1:1), cyclohexanone (1:1), dioxane (1:1), carbon tetrachloride (1:1), 1,1-dichloroethane (1:1), 1,1,2,2-tetrachloroethane (1:1), benzene (1:1), *o*-xylene (1:1), *p*-xylene (2:1), anisole (2:1), *m*-dimethoxybenzene (2:1) and 2-picoline (1:1) showed photochromism in the solid state. Interestingly, the photochromism of



the inclusion crystals of **1** was very sensitive to the structure of the guest compounds. For example, cyclopentanone shows photochromism, while pentan-3-one does not. Similar structural effects were observed in the following cases: dioxane vs. tetrahydropyran, 1,1-dichloroethane vs. 1,2-dichloroethane, *o*-dimethoxybenzene vs. *m*- and *p*-dimethoxybenzene and 2-picoline vs. 3- and 4-picoline. An electronic effect of the guest compounds may be important, because the dimethoxybenzene derivatives as guest showed photochromism, while dichlorobenzene derivatives did not (Table 1).

It is also remarkable that the stability of the photochromism depends on the type of guest molecule. For example, the bleaching times of the green color which developed upon photoirradiation of the various inclusion crystals of **1** were 3 h (benzene), 4 h (cyclopentanone), 5 h (2-methylpyridine), 6 h (*p*-dimethoxybenzene), 9 h (*m*-dimethoxybenzene), 10 h (cyclohexanone and 1,1-dichloroethane), 12 h (anisole and *o*-xylene), 24 h (*p*-xylene), 164 h (butan-2-one), and 504 h (acetone and dioxane), respectively.

The solid-state IR spectrum of the green crystals was identical with that of the yellow crystals, and no EPR signal developed upon photoirradiation. The photochromic properties of **1** are probably due to π - π interactions owing to its suitable molecular packing in the inclusion crystals, because photoirradiation of **1** in solution did not show any photochromic properties. Further detailed studies of the relationship between crystal structures and photochromic properties of the inclusion complexes of **1** are in progress.

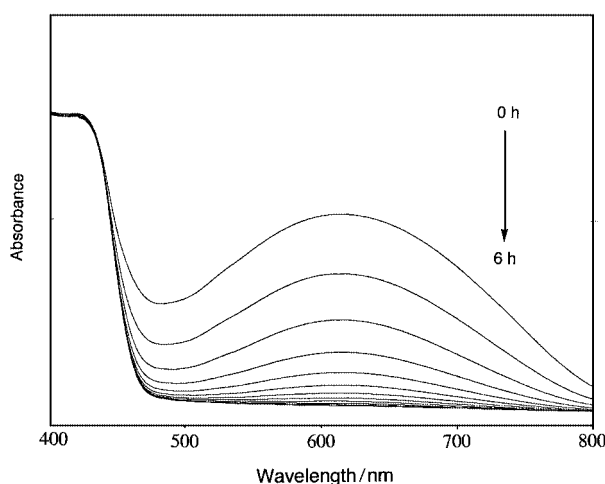























Fig 1 UV spectral changes of the 1:1 inclusion complex of **1** with *p*-dimethoxybenzene in the solid state. Successive measurements were recorded every 30 min from the top (after irradiation) to the bottom (after keeping 6 h in the dark).

Table 1 Inclusion complex of **1** (host:h) with various guest (g) compounds

Guest	h : g ^a	Photochromism	Bleaching time/h	Guest	h : g ^a	Photochromism	Bleaching time/h
Acetone	1 : 1	yes	504		1 : 1	no	
Butan-2-one	1 : 1	yes	164		1 : 1	no	
Pentan-3-one	1 : 1	no			1 : 1	no	
	1 : 1	yes	4		1 : 1	no	
	1 : 1	yes	10		1 : 1	no	
	1 : 1	no			2 : 1	yes	12
	1 : 1	no			2 : 1	no	
	1 : 1	yes	504		2 : 1	yes	9
CH ₂ Cl ₂	1 : 1	no			2 : 1	yes	6
CHCl ₃	1 : 1	no			1 : 1	no	
CCl ₄	1 : 1	yes	9		1 : 1	yes	5
CH ₃ CHCl ₂	1 : 1	yes	10		2 : 1	no	
CH ₂ ClCH ₂ Cl	1 : 1	no			1 : 1	no	
CHCl ₂ CHCl ₂	1 : 1	yes	10				
	1 : 1	yes	3				
	1 : 1	yes	12				
	2 : 1	yes	24				

^a The host : guest ratios were determined by TG, NMR and elemental analysis.

Notes and references

† Representative procedure for preparation of inclusion crystals and measurement of the diffuse reflectance UV spectra: When a mixture of **1**[†] and *p*-dimethoxybenzene was recrystallized from ethyl acetate in the dark, a 2 : 1 inclusion crystal of **1** and *p*-dimethoxybenzene was obtained as pale yellow prisms (mp 165–169 °C). The colored inclusion crystals were developed by photoirradiation with a high-pressure Hg lamp through a Pyrex filter for 10 min under aerobic conditions, and their diffuse reflectance UV spectra monitored by using a Shimadzu MPS-2000 spectrophotometer.

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