Photoreactivities of two kinds of bimolecular crystals formed from acridine and phenothiazine

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A yellow crystal 3 and a red crystal 4 simultaneously crystallize from a solution of acridine 1 and phenothiazine 2 in acetonitrile. Similar N · · · H–N hydrogen bonding pairs of 1 and 2 are formed in the two crystals. The 3:4 crystal 3 has a slightly uncommon molecular arrangement of which four acridine molecules out of twelve are disordered in the unit cell. The 1:1 crystal 4 has a more rigid packing of the hydrogen bonding pairs. Irradiation of 3 gives a photoadduct 5 as the sole product, whereas 4 shows almost no photoreactivity. The occurrence of photoinduced electron transfer has been confirmed by the measurement of transient absorption spectra of the crystals 3 and 4. However, the two-stage decay of the transient absorption of 3 with lifetimes of 2 and 50 ps is different from that of 4 with a single short lifetime of 2 ps. Upon irradiating 3, electron transfer, proton transfer and subsequent radical coupling occur over the shortest distance of 4.1 Å between the preradical carbon and nitrogen atoms in the crystal lattice followed by dehydrogenation to afford the product 5. In the case of the red crystal 4, the radical coupling is difficult because of the longer coupling distance of 5.6 Å and the more restricted movement in the rigid crystal lattice. The results indicate that the observed photochemical behaviour of 3 and 4 are controlled by the molecular arrangement in the crystal lattice.

Since the discovery of topochemical [2 + 2] photocycloadditions by Cohen and Schmidt,[1] a large number of solid state photoreactions of one-component molecular crystals have been reported. However, the reaction types were almost always limited to [2 + 2] cycloadditions and some intramolecular reactions, such as hydrogen abstraction, and so have not extended the scope of solid state organic photochemistry.[2,3] Recently, we have studied the photochemistry of two-component molecular crystals prepared by the self-assembly of different organic molecules[4] and developed several bimolecular reactions that occur in the crystal lattice.[5–9] An important advantage to utilizing a bimolecular crystal as a reaction medium is that induction of reactivity is possible *via* photoinduced electron transfer (PET) by combining an electron donor and acceptor species. Although a large number of PET reactions are already known in solution photochemistry, the product selectivities are low due to the high mobility of radical species in the solutions.[10] In contrast, solid state PET reaction can give high product selectivity due to the quite low mobility in the crystal lattice, as in photodecarboxylation of bimolecular crystals of indole-3-acetic acid and phenanthridine, for example.[6] The occurrence of a stereospecific reaction ultimately results in the success of absolute asymmetric synthesis.[9,11,12] Namely, solid state bimolecular photoreactivity depends not only on the nature of component molecules but also on the crystal structure.

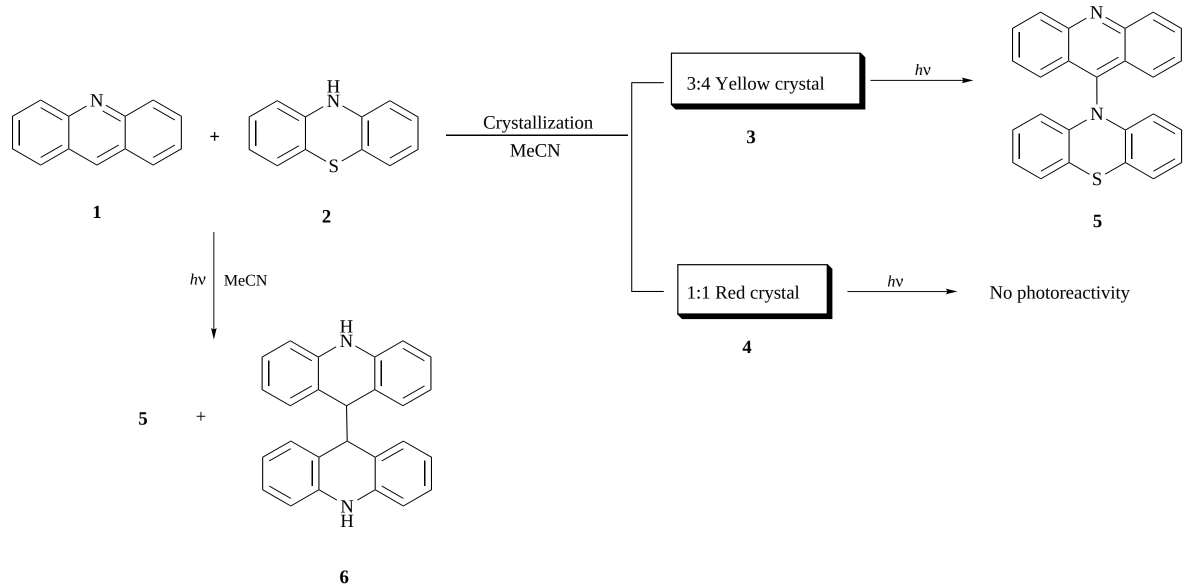
Here, we report an interesting case of two kinds of bimolecular crystals **3** (yellow) and **4** (red) that are formed simultaneously from solutions of acridine **1** and phenothiazine **2**. Irradiation of **3** causes photoaddition, while **4** has almost no photoreactivity. Further, we describe the first evidence for the occurrence of solid state PET by the successful measurement of transient absorption spectra in femtosecond diffuse reflectance spectroscopy.[13,14] The correlation between the molecular arrangement and photoreactivity of the two crystals is discussed.

Results and discussion

Crystal structure

The 3:4 yellow crystal **3** and the 1:1 red crystal **4** are simultaneously crystallized from an equimolar solution of acridine **1** and phenothiazine **2** in acetonitrile. By seeding the desired crystals they can be prepared on a large scale. The ground-state absorption spectra of the microcrystals **3** and **4** were measured by a reflection method using $MgSO_4$ as a standard (Fig. 1). Although the yellow and red colours of the single crystals are visually very different, the two spectra seem to be quite similar at longer wavelengths. The melting point of **3** is 134 °C, falling between those of **1** (107 °C) and **2** (185 °C). The red colour of **4** changes to yellow at around 90 °C, which is a transition point, and the crystal melts at 134 °C, corresponding to the two endothermic peaks in DSC measurements. The powder X-ray diffraction (PXD) pattern of **3** is almost the same as that of 1:1 melting–resolidifying mixture of **1** and **2**. When **4** was submitted to melting–resolidifying manipulation, the PXD pattern changed to be almost concordant with that of the 1:1 melting–resolidifying mixture of **1** and **2**. It indicated that **4** can form only by crystallization from solution. The simultaneous crystallization of **3** and **4** from solution suggests that the difference in their formation energies is small; thermodynamics studies are under way.

Table 1 shows the X-ray crystal structure data for crystals **3** and **4** and product **5**. It should be noted that crystals **3** and **4** have centrosymmetric space groups, $C2/c$ and $P2_1/c$, respectively, while phenothiazine crystal is known to have an enantiomorphous space group $P2_1$.[15] Crystalline **3** has a relatively



Scheme 1

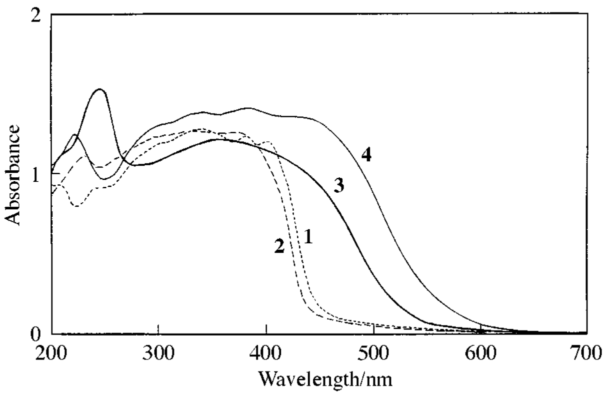


Fig. 1 Ground-state absorption spectra of **3** and **4** and components **1** and **2**

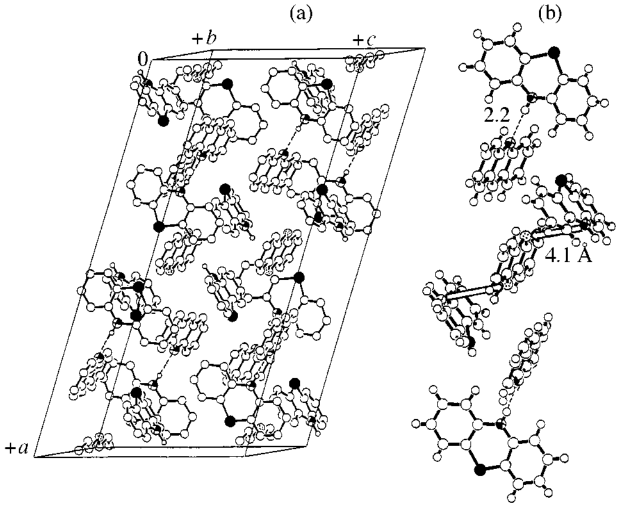


Fig. 2 (*a*) Molecular packing and (*b*) the radical coupling path in **3**. In (*a*), the hydrogens are omitted except for the NH hydrogens for clarity. Sulfur (●) and nitrogen ⊕. Dotted atoms in the disordered acridine molecules represent the coexistence of carbon and nitrogen atoms with occupancies of about 50%.

uncommon molecular arrangement in which twelve and sixteen molecules of **1** and **2**, respectively, are packed in the unit cell (Fig. 2). The molecular shape of **1** is almost flat, but that of **2** is butterfly-like due to the longer S–C bond (1.8 Å) than C–N and C–C bonds (1.4 Å). Molecular pairs of **1** and **2** are formed through N · · · H–N hydrogen bonding with H · · · N distance of 2.15 Å; the dihedral angle between the plane of **1** and the central C–C–C–C plane of **2** is 86.58°, *i.e.* almost perpendicular. The eight molecular pairs of **1** and **2** are packed head-to-tail with a distance of 6.4 Å between the two acridine planes in the crystal lattice. The eight molecules of each of **1** and **2** are arranged almost parallel to the *ab* face and the *ac* face, respectively. The residual four acridine molecules out of twelve are disordered, in which N and C atoms coexist at about 50% occupancy (Fig. 2). The four disordered acridine molecules and the residual eight phenothiazine molecules do not form hydrogen bonds in the unit cell. The disordered acridine is placed between the two phenothiazine molecules at a dihedral angle of 58.2°. Further, the acridine molecules with and without hydrogen bonds are arranged almost parallel to each other (dihedral angle 5.15°). On the other hand, the phenothiazine molecules with and without hydrogen bonds are almost perpendicular (dihedral angle 89.38°). The IR absorption band of **3** at 3342 cm^{-1} corresponds to the molecules of **2** with no hydrogen bonds in **3** in good accordance with the NH band of the crystal **2**. The bands at 3391, 3237 and 3164 cm^{-1} correspond to the N · · · H–N hydrogen bonds of **1** and **2**.

In crystalline **4**, similar hydrogen bonding pairs are formed with an H · · · N distance of 2.19 Å; the dihedral angle between the plane of **1** and the central C–C–C–C plane of **2** is 85.73° (Fig. 3). The IR absorption bands of **4** at 3395, 3240 and 3179 cm^{-1} correspond to the N · · · H–N hydrogen bonding, but are slightly shorter than those of **3**. Four molecular pairs exist in the unit cell. The molecular pairs are arranged head-to-tail to form two independent stacking columns (A) and (B) with plane distances of 3.9 and 8.9 Å between the two acridine molecules in the crystal lattice. The phenothiazine molecules in column (A) are arranged almost perpendicular to the acridine planes in the next stacking column (B) with the shortest distance of 2.9 Å between the aromatic H atom of **2** and the acridine plane. Such rigid molecular packing is a feature of crystal **4**.

Photoreactions

Crystals were pulverized and irradiated with a 400 W high-pressure mercury lamp through Pyrex glass (>290 nm transparent) under argon. Scheme 1 and Table 2 show the results together with the solution photoreaction. Irradiation of **3** caused an addition reaction to give photoadduct **5** in low yield as the sole product. The molecular structure of **5** was confirmed

Table 1 X-Ray crystallographic data for the bimolecular crystals and the product

	Yellow crystal **3**	Red crystal **4**	Product **5**
Formula	$C_{87}H_{63}N_7S_4$	$C_{25}H_{18}N_2S$	$C_{25}H_{16}N_2S$
M_w	1334.74	378.49	376.47
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/n$
Z	4	4	4
Cell constants			
a/Å	30.194(3)	13.121(2)	8.460(8)
b/Å	14.686(3)	9.126(3)	9.870(2)
c/Å	15.996(3)	17.318(2)	22.633(7)
β/°	107.930(9)	110.83(1)	99.39(6)
V/Å^3	6748(1)	1938.1(8)	1864(2)
D_c/g cm^{-3}	1.314	1.297	1.341
μ/cm^{-1}	17.16	1.79	1.86
Radiation	Cu-Kα	Mo-Kα	Mo-Kα
$2\theta_{max}$/°	120.3	50.0	50.0
Scan mode	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
No. of reflections measured	5367	3809	3745
No. of unique reflections	5252	3642	3493
No. with $I > 3.00\sigma(I)$	4540	2583	1006
No. of variables	566	257	254
R (%)	8.9	5.6	5.6
R_w (%)	8.0	8.0	7.5

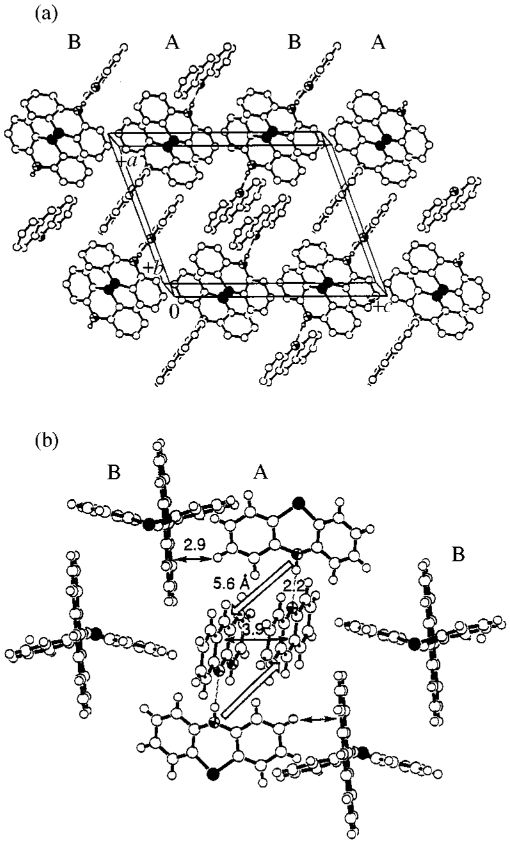


Fig. 3 (*a*) Molecular packing and (*b*) the radical coupling path in **4**. In (*a*), the hydrogens are omitted except for the NH hydrogens for clarity. Sulfur (●) and nitrogen ⊕. (A) and (B) are the independent molecular stacking columns.

by X-ray structure analysis (Fig. 4). However, **4** showed much lower photoreactivity and afforded no isolated product. The difference in photoreactivities between **3** and **4** can be attributed to the difference in crystal structures because both crystals consist of the same components **1** and **2**. For a comparison, irradiation of a solution of **1** and **2** in acetonitrile produced **5** and biacridine **6** in 64 and 35% yield, respectively.

Table 2 Photoreaction of acridine and phenothiazine in bimolecular crystals and in solution

State on irradiation	Conversion (%)		Yield[a] (%)	
	1	**2**	**5**	**6**
Yellow crystal **3**	8	15	14	0
Red crystal **4**	3	7	0	0
MeCN soln	16	50	64	35

[a] Yield based on consumed **1**.

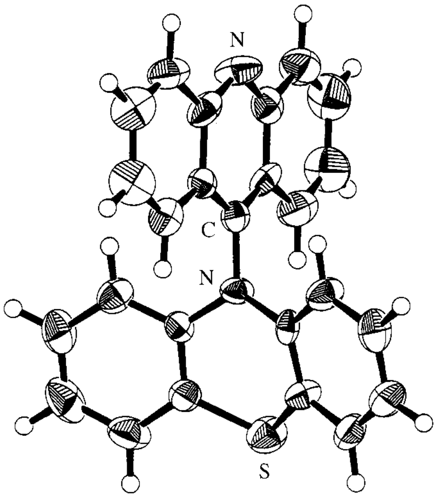


Fig. 4 Molecular structure of product **5**

The transient absorption spectra of the yellow microcrystals **3** are shown in Fig. 5. The absorption bands with maximum wavelengths at around 600 and 520 nm were observed immediately after excitation with a 390 nm laser pulse. They could be assigned to the absorption spectrum of acridine anion radical and that of the phenothiazine cation radical, respectively, on the basis of the similarity to those in solution.[16] This result provides direct evidence for the generation of ionic species in a photoreactive two-component crystal. The decay of transient absorption in Fig. 6 shows non-exponential behaviour, and it can be approximated to by a double-exponential function with lifetimes of 2 and about 50 ps. Since almost the same decay was observed even at a half the excitation intensity, the observed decay may be mainly ascribed to geminate recombination of charge-separated species but not bulk recombination of them. Most probably it reflects the uncommon molecular arrangement in the crystal lattice of **3**, for instance disordered

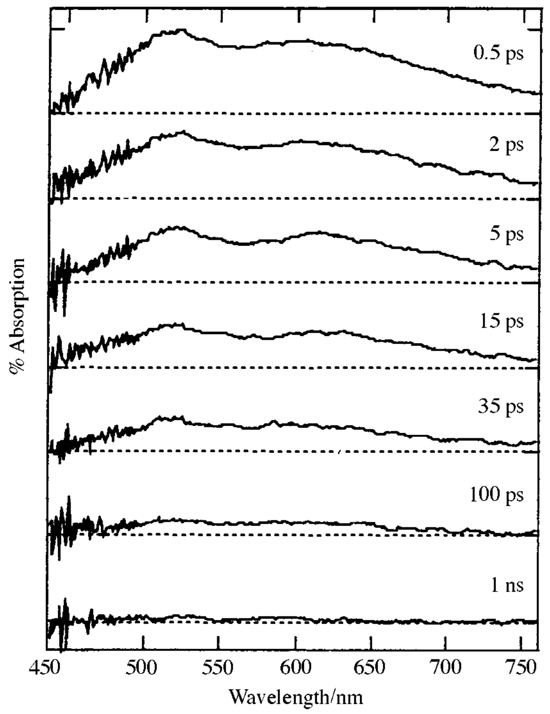


Fig. 5 Transient absorption spectra of **3** excited at 390 nm

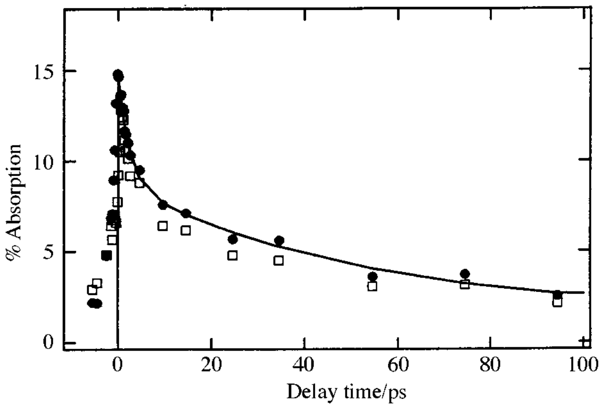
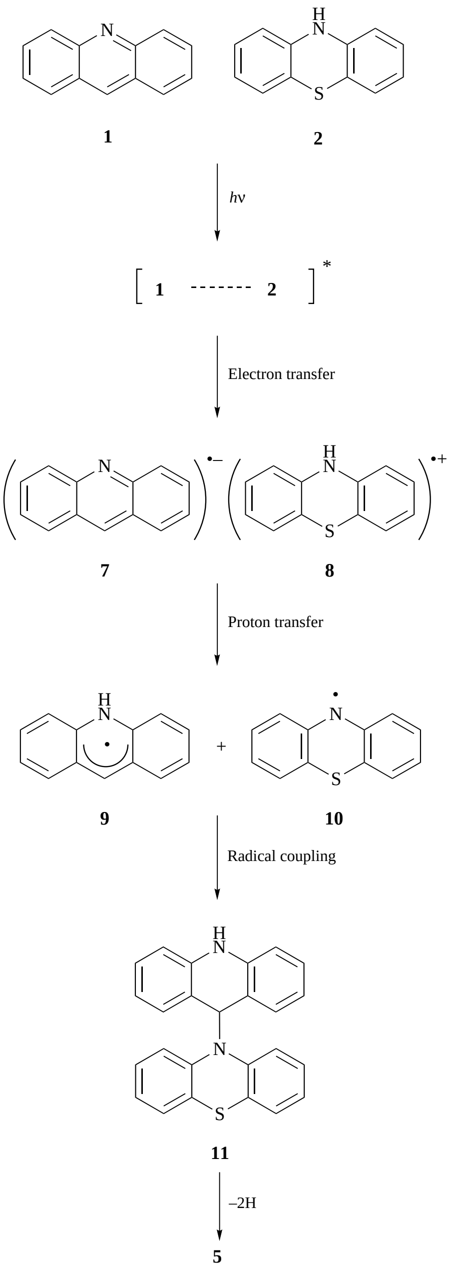


Fig. 6 Observed time profiles of the transient absorption of **3**. Probe wavelengths are at 524 nm (●) and 613 nm (□). Solid lines are calculated curves by eqn. (2) in ref. 14: $n(t) = 5.8\exp(-t/2.5\ \mathrm{ps}) + 7.5\exp(-t/50\ \mathrm{ps}) + 1.4$.

acridine molecules and the coexistence of hydrogen bonding and non-hydrogen bonding pairs.

In the case of red microcrystals of **4**, similar transient absorption spectra to those of the yellow crystals were observed, but the decay was approximated to by a single exponential decay with a lifetime of about 2 ps and no transient absorption was observed after several tens of picoseconds. The fast decay components observed for the two crystals are probably due to the charge-transfer (CT) excited state of the hydrogen bonding pair. Compared with the CT excited state of some typical crystals of weak CT complexes,[14] this lifetime is very short. It is suggested that hydrogen-bonding is the key role in the ultrafast deactivation of the excited state. The details of the dynamics and the mechanisms will be discussed elsewhere. On the other hand, a slow deactivation observed only for the yellow crystals corresponds to a charge separated species formed between the non-hydrogen bonding pairs. If we consider that a part of them results in the formation of photoproduct **5** then the above results for transient absorption measurements are quite consistent with the different photoreactivities of the yellow and red crystals.



Scheme 2

Scheme 2 shows the possible reaction mechanism based on the transient absorption spectra and the photoproduct **5**. Upon irradiation, PET from **2** to **1** occurs to give the acridine anion radical **7** and the phenothiazine cation radical **8**. Then proton transfer produces the hydroacridine radical **9** and the dehydrophenothiazine radical species **10**. In the case of the crystalline **3** [Fig. 2(*b*)], radical coupling between **9** and **10**, which originates from the disordered acridine and non-hydrogen bonding phenothiazine, can occur over the shortest distance of 4.14 Å most effectively and is followed by dehydrogenation to give product **5**. Occurrence of radical coupling between the hydrogen bonding pair is difficult because a half rotation of **9** is needed in the crystal lattice. The low yield of **5** (Table 2) is most probably due to the existence of only four disordered acridine molecules out of twelve in the unit cell.

On the other hand, the lack of production of **5** on irradiation of **4** should be attributed not only to the short lifetimes of the radical species but also to the molecular arrangement in the crystal lattice. The distance of 5.58 Å for the radical coupling of **9** and **10** in Fig. 3(*b*) can be said to be short enough for radical coupling because an even longer distance of 6.8 Å causes radical coupling in other bimolecular crystals.[9] Steric hindrance may also be a reason for the non-occurrence of radical coupling. In Fig. 3(*a*), the plane distance between two acridine molecules in column (A) is 3.9 Å. On the other hand, the phenothiazine molecule of the stacking column (A) is close to the acridine molecule of the next stacking column (B) with the shortest distance (2.9 Å) between the H atom of phenothiazine and the acridine plane. Therefore, radical **10** cannot move to radical **9** in the crystal lattice. Such a rigid molecular packing arrangement leads to no production of **5**. The reason for the lower conversion of **1** compared to **2** is the regeneration of **1** by dehydrogenation of the radical **9** (Table 2).

Conclusions

Spontaneous crystallization of two kinds of bimolecular crystals occurs from the acetonitrile solution of acridine phenothiazine. Irradiation of **3** gives the photoadduct **5** as the sole product. On the other hand, **4** has a much lower photoreactivity. Transient absorption spectra of the microcrystals could be measured by femtosecond diffuse reflectance spectroscopy and provide the first evidence for a photoinduced electron transfer reaction in a bimolecular crystal. The difference in reactivities between the two crystals could be explained by their molecular arrangements in the crystal lattice.

Experimental

Instrumentation

^{1}H NMR spectra were measured on a 60 MHz JEOL spectrometer with tetramethylsilane as an internal standard. IR spectra were recorded on a JASCO FTIR-8300 spectrophotometer. UV spectra were measured on Shimadzu UV-3100 and MPS 2000 spectrophotometers. Powder X-ray diffractograms (PXD) were taken on a Rigaku Geigerflex by using Cu-target X-ray tube equipped with a RAD-C system. Differential scanning calorimetry (DSC) was done on a Rigaku Thermoflex TAS-200 DSC8230D and melting points were uncorrected. Elemental analysis was carried out with a Yanaco CHN Corder MT-5. HPLC with a photodiode-array detector was used to determine the products on a Waters HPLC system.

Preparation of bimolecular crystals 3 and 4

Acridine **1** (GR grade, Tokyo Kasei) was recrystallized from ethanol. Phenothiazine **2** (GR grade, Tokyo Kasei) was used as received. Yellow crystals of **3** and red crystals of **4** were prepared by slow evaporation of a 1:1 solution of **1** and **2** in acetonitrile at room temp. by seeding.

Crystals of **3**; mp 133–135 °C [Found: C, 79.74; H, 5.05; N, 7.39. Calc. for $C_{87}H_{63}N_7S_4$ (3:4): C, 78.29; H, 4.76; N, 7.35%]; ν_{max}(KBr)/cm^{-1} 3342 (NH of **2**), 3391, 3237 and 3164 (N···HN); λ(solid state)/nm 190–550.

Crystals of **4**; transition point about 90 °C; mp 133–135 °C [Found: C, 79.30; H, 4.93; N, 7.42. Calc. for $C_{25}H_{18}N_2S_1$ (1:1): C, 79.34; H, 4.79; N, 7.40%]; ν_{max}(KBr)/cm^{-1} 3395, 3240 and 3179 (N···HN); λ(solid state)/nm 190–600.

Preparative photoreaction of 1 and 2 in MeCN

A solution containing **1** (0.895 g, 5 mmol) and **2** (0.996 g, 5 mmol) in acetonitrile (100 cm^3) was irradiated internally with a 100 W high-pressure mercury lamp under argon for 45 h at room temp. followed by filtration to give biacridane **6** (0.052 g, 5.6%) as a solid, mp 211–212 °C (from tetrahydrofuran) (Found: C, 86.76; H, 5.76; N, 7.85. Calc. for $C_{26}H_{20}N_2$: C, 86.64; H, 5.59; N, 7.77%); ν_{max}(KBr)/cm^{-1} 3370 (NH), consistent with an authentic sample. After evaporation of the filtrate, the residue was chromatographed using a silica gel plate (5% ethyl acetate–hexane) to give the condensation product **5** (0.195 g, 10.3%), mp 289–291 °C (from MeCN) (Found: C, 79.80, H, 4.41; N, 7.46. Calc. for $C_{25}H_{16}N_2S$: C, 79.76; H, 4.28; N, 7.44%); ν_{max}(KBr)/cm^{-1} no NH; δ_H(60 MHz, [$^2H_8$]THF) 5.82–5.67 (2H, m, Ph), 7.14–6.44 (6H, m, Ph), 7.96–7.41 (4H, m, Ph) and 8.39–8.20 (4H, m, Ph); λ_{max}/nm (10% THF in MeCN) 384 (log ε, 3.79), 362 (4.11), 345 (3.97) and 252 (5.16). The molecular structure was confirmed by X-ray crystallographic analysis (Fig. 4).

Solid-state photoreaction of 3 and 4

Crystals of **3** and **4** (20 mg) were pulverized in a mortar and placed between two Pyrex glass plates and irradiated with a 400 W high-pressure mercury lamp (>290 nm irradiation) under argon at 15 °C for 24 h followed by HPLC analysis using a C_{18} column (methanol–water). The results are shown in Scheme 1 and Table 2.

X-Ray crystallography

Experimental details of the structure determination of **3**, **4** and **5** are presented in Table 1. Data collections were performed on a Rigaku AFC7R automatic four-circle X-ray diffractometer with graphite monochromated Cu-Kα (λ = 1.541 78 Å) Mo-Kα (λ = 0.710 69 Å) radiation and a rotating anode.† The structure was solved by direct method (SHELXS-86) and refined by full-matrix least squares analysis. The non-hydrogen atoms were refined anisotropically. All the calculations were carried out on the teXsan crystallographic software package from Molecular Structure Corporation.

Measurement of transient absorption spectra

The details of a femtosecond diffuse reflectance spectroscopic system have been reported.[13] Briefly, an excitation light source consisting of a continuous wave self-mode-locked Ti:sapphire laser (Mira 900 Basic, Coherent), pumped by an Ar$^+$ laser (Innova 310, Coherent), and a Ti:sapphire regenerative amplifier system (TR70, Continuum) with a Q-switched regenerative amplifier (780 nm, 3–4 mJ/pulse, 170 fs fwhm, 10 Hz) was frequency doubled (390 nm) and used as an excitation light source. The residual of the fundamental output was focused into a quartz cell (1 cm path length) containing H_2O to generate a white-light continuum as a probe beam.

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† Atomic co-ordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See ‘Instructions for Authors’, *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/87.

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