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SPECIFIC HOST-GUEST ENERGY TRANSFER BY USE OF β-CYCLODEXTRIN RIGIDLY CAPPED WITH A BENZOPHENONE MOIETY

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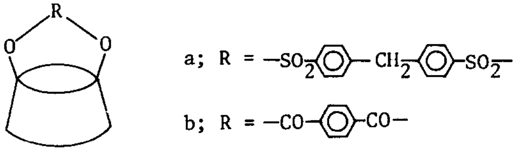
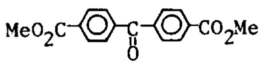
Energy transfer between a donor and an acceptor in photochemistry has been well docummented[1]. In triplet-triplet energy transfer, the efficiency of an acceptor or a donor is usually determined by the triplet energy levels, although the importance of simple steric repulsion between a donor and an acceptor was also pointed out in some cases[2]. During the past decade, the molecular structure recognition by host-guest interaction in (one to one) inclusion has attracted much attention and even simple compounds, such as cyclodextrins[3] or crown ethers[4], were shown to recognize the molecular geometry of guest molecules. Our recent finding that the rigid[5] capping on cyclodextrin with diphenylmethanedisulfonate or terephthalate (1a or 1b) causes a remarkable increase in the association constant of β-cyclodextrin moiety for hydrophobic guests[6] prompted us to explore a novel type of capping with hydrophobic cavity which may operate as a specific sensitizer or quencher for a guest of appropriate shape in ground or excited state, respectively. In this communication, we wish to report the pre-



1a,b



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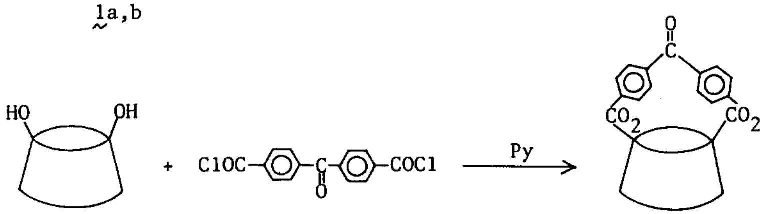

4 2

Scheme 1.

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paration of a novel type of inclusion host molecule, cyclodextrin capped with benzophenone moiety, 2, and that the selective inclusion can cause the (structurally) specific and very effective triplet energy transfer between the excited host and ground guest molecules. This is a novel type of energy transfer allowed only for host-guest of exact structural recognition.

Donor esters, cyclodextrin rigidly capped with a benzophenone chromophore (2) and its open-chain analog 3, were prepared from 4,4'-bis(chlorocarbonyl)benzophenone and β-cyclodextrin, 4, or methanol, respectively[7] (Scheme 1). Compounds, 5 and 6, were chosen as triplet energy acceptors since selective excitation of the donor, 2 (E_S=81 kcal/mole, E_T=66 kcal/mole)[8] or 3 (E_S=81 kcal/mole, E_T=67 kcal/mole)[9a] can be achieved by 353 nm or 370 nm irradiation, respectively, without excitation of the acceptors, 5 and 6[8,9,10]. A typical example of the observed phosphorescence spectra is shown in Fig. 1 for the donor-acceptor combination of 2+5 measured at liquid nitrogen temperature. The effective triplet-triplet energy transfer from 2 (3.3×10^{-4} M) to 5 (5.0×10^{-4} M) was successfully observed even in this considerably unfavorable (low) concentration for the transfer where the open-chain analog, 3 (1.2×10^{-3} M), did not show any appreciable energy transfer to 5 (2.4×10^{-3} M). This unusually

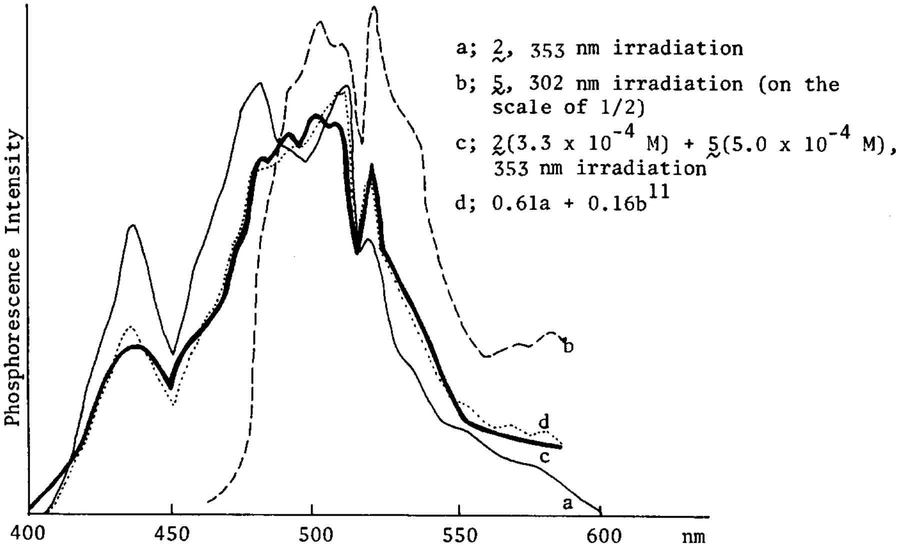
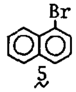
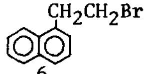
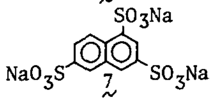


Figure 1. Phosphorescence spectra(corrected) of 2(a), 5(b), and 2+5(c) (77°K, 25% aq. DMF). The observed spectrum (c) can be reproduced by superposition (d) of two components, (a) and (b)[11].

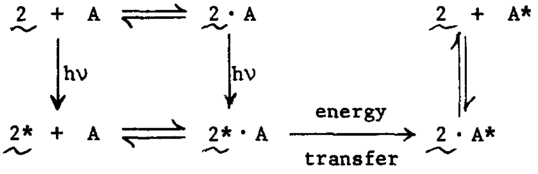
Table 1. Energy Transfer from Triplet Excited State of Capped Cyclodextrin 2 or Linear Analog 3 to Acceptor[a)]

Acceptor	E_T kcal/mole	Quenching Efficiency of Phosphorescence of Donor, $(\phi_0^D-\phi_A^D)/\phi_0^D$ b)		Apparent Efficiency of Energy Transfer from 2 $\phi^A/(\phi_0^D-\phi_A^D)$ b)
		2	3	
 5	$59^{c)}$	$39\%^{d)}$	$0\%^{e)}$	60%
 6	$59^{f)}$	$35\%^{d)}$	$0\%^{d)}$	50%
 7	$55^{f)}$	$0\%^{g)}$	$0\%^{g)}$	—

a) solvent; 25% aq. DMF, temperature; 77°K b) ϕ_0^D or ϕ_A^D is the phosphorescence quantum yield of the donor in the absence or the presence of an acceptor, respectively. ϕ^A is the phosphorescence quantum yield of the acceptor after the energy transfer. See footnote 11. c) See footnote 9a,b. d) 2; 3.0×10^{-4} M, 5,6; 5.0×10^{-4} M e) 2; 1.2×10^{-3} M, 5; 2.4×10^{-3} M f) See footnote 8. g) 2; 3.0×10^{-4} M, 7; 5.0×10^{-3} M

effective energy transfer is rather general for the guest acceptors of appropriate shapes for the binding by the capped β-cyclodextrin according to our preliminary experiments. Thus the marked and interesting difference in the transfer efficiency of the donors, 2 and 3, shown in Table 1 is also interpreted by the host-guest interaction by the capped β-cyclodextrin cavity which is recently reported to form inclusion compounds with naphthalene, or sodium 8-anilino-1-naphthalenesulfonate[6]. This remarkable significance of the guest binding by the host cavity to the effective transfer was also shown by the absence of the energy transfer from 2 (3.0 x 10^{-4} M) to trisodium naphthalene-1,3,6-trisulfonate 7 (5.0 x 10^{-3} M), which is a very hydrophilic and inappropriately shaped guest.

Thus, the general scheme of this specific energy transfer would be described in Scheme 2. This inclusion-energy transfer combination, a new type of specific energy transfer, is applicable to reactions in solution according to our preliminary experiments and the enhanced and specific isomerization of olefins is now extensively investigated.



A: Acceptor.

2 · A: Inclusion complex.

Scheme 2.

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7) Treatment of β-cyclodextrin (0.0013 mole) with 4,4'-bis(chlorocarbonyl)benzophenone (0.0013 mole) in pyridine (200 ml) followed by concentration, reprecipitation and preparative thin layer chromatography gave the pure capped β-cyclodextrin; ir (KBr), 1720, 1650 and 1275 cm^{-1}; NMR (DMSO-d_6), δ, 8.14 and 7.85 (AB quartet, $J = 8$ HZ, 8 H, aromatic H), 4.84 (multiplet, 7 H, C_1-H), and 3.68 (multiplet, others).

8) E_T and E_S were estimated from the phosphorescence and the absorption spectrum, respectively.

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11) From the relative phosphorescence quantum yields of **2** and an acceptor (**5**—**7**), the efficiency was estimated, under the present condition of host-guest combination, based on the assumed phosphorescence quantum yield of **2** to be 0.8.$^{a)}$

a) Benzophenone, 0.84, 0.74, 4,4'-dimethylbenzophenone, 0.86 at 77°K; see(9b) pp.41.