Crystal Structure of Light-induced Colored Species from Photochromic Dimer of 1,4-Bis(imidazolyl)tetrafluorobenzene

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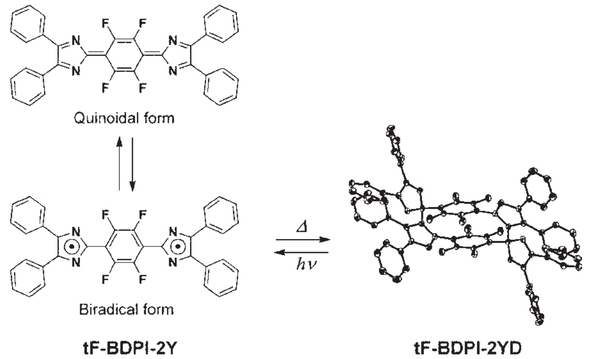
On irradiation with UV light, the photochromic dimer of 1,4-bis(imidazolyl)tetrafluorobenzene produced the colored transient species in solution and solid. Though the dimerization reaction to form the photochromic dimer prevents the isolation and characterization of the colored species at room temperature, the single crystals of the colored species could be successfully obtained from the light-irradiated toluene solution of the dimer at 200 K, and the molecular structure of the colored species is unambiguously determined by the X-ray diffraction analysis.

Hexaarylbiimidazoles (HABIs) are known as a family of organic photochromic compounds and are readily cleaved, both thermally and photochemically, into a pair of triarylimidazolyl radicals that can reversibly recombine to form the imidazole dimer.[1] On the other hand, the bisimidazolyl radical, 1,4-bis-(4,5-diphenylimidazol-2-ylidene)cyclohexa-2,5-diene (BDPI-2Y), would not form an imidazole dimer. The presence of the thermal equilibrium between a diamagnetic quinoidal state and a paramagnetic-biradical state in both solid and solution had been considered for the reason of this significant behavior, nevertheless, a definitive evidence for the presence of a biradical state had not been demonstrated.[2] Controlling the equilibrium between a closed-shell quinoidal state and an open-shell biradical state will provide a significant progress in the field of the biradical chemistry, and especially in the field of the π-conjugated delocalized biradical chemistry. Though only 0.1% of BDPI-2Y in solution lies to the paramagnetic state at room temperature, we have succeeded to increase in the population of the biradical species by the chemical modification with a suitable substituent. In our previous paper, we have described a novel BDPI-2Y derivative, tF-BDPI-2Y, substituted four hydrogen atoms at the central phenylene ring of BDPI-2Y with fluorine atoms (Scheme 1).[3] The increase in the population of paramagnetic species of tF-BDPI-2Y (0.4%) compared with BDPI-2Y (0.1%) in solution was achieved, and as is distinct from BDPI-2Y, tF-BDPI-2Y shows the radical recombination reaction to form a photochromic HABI derivative, tF-BDPI-2YD. This gives the definitive evidence for the contribution of biradical character in tF-BDPI-2Y. While the molecular structure of tF-BDPI-2YD could be successfully determined by X-ray diffraction, the isolation and determination of the molecular structure of tF-BDPI-2Y has been making it the subject of considerable study. In this communication, we will describe the crystallization and X-ray diffraction study for the light-induced transient species from a photochromic tF-BDPI-2YD.



Scheme 1. Reversible photodissociation of tF-BDPI-2YD into two tF-BDPI-2Ys and thermal equilibrium in tF-BDPI-2Y.

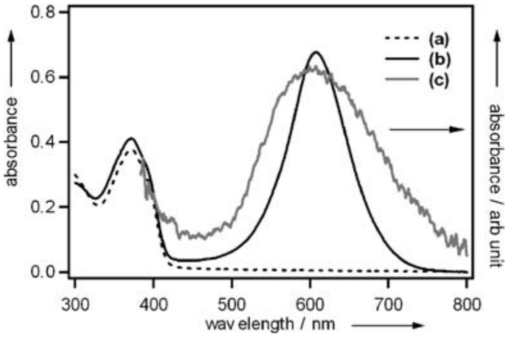


Figure 1. Absorption spectra of tF-BDPI-2YD in benzene (6.25×10^{-6} M) (a) before irradiation, (b) immediately after irradiation with 360 nm light at room temperature, and (c) the crystalline precipitates obtained from the light-irradiated toluene solution of tF-BDPI-2YD (right axis). All the measurements in solution were carried out by using a 10 mm cell.

On irradiation with 360 nm light, the colorless benzene solution of tF-BDPI-2YD quickly turned to blue-purple and gave rise to a broad absorption band centered at 609 nm. On standing in the dark, the blue-purple color gradually faded with the decrease in the absorbance in visible light region. Thermal back reaction to form tF-BDPI-2YD was observed over a period of two days at 293 K in the dark, indicating that the light-induced colored species are stable in solution at room temperature. We could tentatively assigned the colored species to tF-BDPI-2Y from the similarity in the UV–vis absorption spectrum to that of BDPI-2Y, and from the experimentally determined spin concentration based on the ESR signal intensity.[3] Though these results may support the formation of tF-BDPI-2Y with biradical character, the possibility for the presence of radical species obtained by a single C–N bond scission could not be excluded. Attempts to recrystallize the resulting colored species from the concentrated benzene solution at room temperature were unsuccessful and gave only the colorless crystals of tF-BDPI-2YD. Because of the fact that the dimerization of radical species follows the sec-

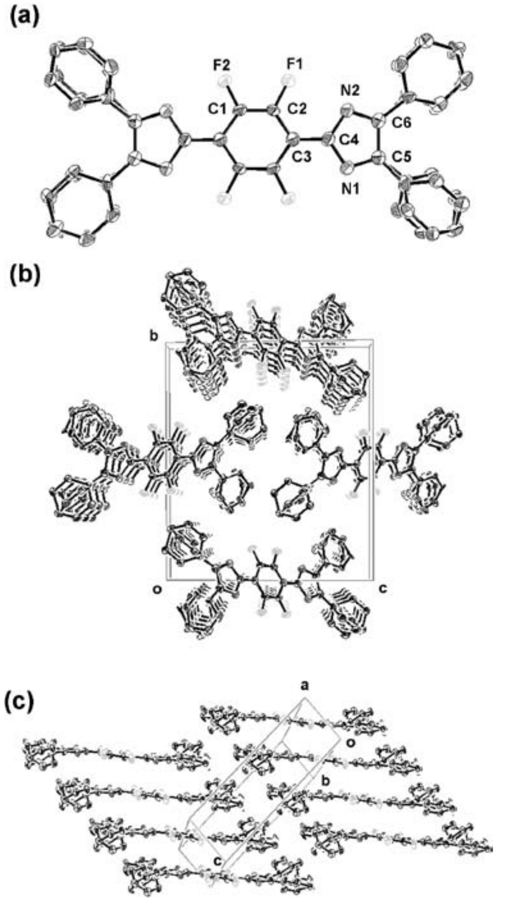


Figure 2. (a) Perspective view of tF-BDPI-2Y. The ellipsoids are drawn at the 30% probability level. tF-BDPI-2Y crystallizes with disorder with respect to the four phenylene rings. The hydrogen atoms are not shown for clarity. Selected distances (Å): C1–C2, 1.344(6); C2–C3, 1.423(6); C3–C4, 1.407(6); C4–N1, 1.390(6); C4–N2, 1.385(6); N1–C5, 1.319(6); N2–C6, 1.328(6); C5–C6, 1.494(7); C1–F2, 1.348(4); C2–F1, 1.350(4). (b) Crystal packing of tF-BDPI-2Y viewed down the crystallographic *a* axis. (c) Slipped stacks of tF-BDPI-2Y.

ond-order kinetics, the increase in the concentration of radical species would lead to the formation of the imidazole dimer in a nonlinear manner. However, an activation energy barrier should exist toward a formation of a dimer structure from two radical molecules. Indeed the suppression of the dimerization reaction of the light-induced radical pair in a single crystal of *o*-Cl-HABI was confirmed below 180 K by the X-ray diffraction study.[1c,1d] Irradiation with 360 nm light at 200 K on the saturated colorless toluene solution of tF-BDPI-2YD produced a blue-purple color, and gave crystalline precipitates as deep greenish-blue fine prisms with metallic luster. The UV–vis absorption spectrum of a benzene solution of the precipitate is identical to that obtained by the light-irradiated benzene solution of tF-BDPI-2YD, and the blue-purple color gradually faded with the decrease in the absorbance in visible light region. Moreover, the absorption spectrum of the crystalline precipitate in solid state is comparable to that measured in solution as shown in Figure 1. These observations give strong support for the assumption that the precipitates correspond to the light-induced species.

We have carried out the X-ray diffraction study for the crystal of the light-induced colored species at 100 K.[4] The molecular structure of the colored species was unambiguously determined as shown in Figure 2. As would be expected, it has become apparent that the colored species corresponds to tF-BDPI-2Y. Though the dimerization reaction to form tF-BDPI-2YD at room temperature prevents the isolation and characterization of tF-BDPI-2Y, it is noteworthy that the crystals of tF-BDPI-2Y could be successfully obtained from the light-irradiated toluene solution of tF-BDPI-2YD at 200 K. The crystals are stable to air and light without leading to the dimerization reaction in solid. The imidazolyl rings and the central tetrafluorophenylene ring are almost coplanar, and the dihedral angle for C2–C3–C4–N2 is about 3.4°. The molecules form strongly slipped stacks along the *a* axis as shown in Figure 2c, and the mean interplanar separation between consecutive molecules along the stacking direction is 3.22 Å. Comparing with the molecular structure of tF-BDPI-2YD determined by X-ray diffraction,[3] in which the central tetrafluorophenylene ring takes a nearly regular hexagonal structure and the averaged C–C bond distance in the ring is 1.39 Å, the C1–C2 bonds become shorter while the C2–C3 bonds are longer in tF-BDPI-2Y. This structure could be considered as 1,4-quinoid-like structure and is consistent with the optimized structure for the singlet ground state of tF-BDPI-2Y calculated by the DFT B3LYP/6-31G(d) method.[3]

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References and Notes

1 a) T. Hayashi and K. Maeda, *Bull. Chem. Soc. Jpn.*, **33**, 565 (1960). b) D. M. White and J. Sonnenberg, *J. Am. Chem. Soc.*, **88**, 3825 (1966). c) M. Kawano, T. Sano, J. Abe, and Y. Ohashi, *J. Am. Chem. Soc.*, **121**, 8106 (1999). d) J. Abe, T. Sano, M. Kawano, Y. Ohashi, M. M. Matsushita, and T. Iyoda, *Angew. Chem., Int. Ed. Engl.*, **40**, 580 (2001). e) A. Kikuchi, T. Iyoda, and J. Abe, *Chem. Commun.*, **2002**, 1484.

2 a) U. Mayer, H. Baumgärtel, and H. Zimmermann, *Angew. Chem.*, **78**, 303 (1966). b) Y. Sakaino, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 1063. c) R. Gompper, M. Mehrer, and K. Polborn, *Tetrahedron Lett.*, **34**, 6379 (1993).

3 A. Kikuchi, F. Iwahori, and J. Abe, *J. Am. Chem. Soc.*, **126**, 6526 (2004).

4 The preparation of tF-BDPI-2Y was described in the ref 3. Crystal structure data for tF-BDPI-2Y: $C_{36}H_{20}F_4N_4$, $M_r = 584.18$, monoclinic, space group $P2_1/n$, $\lambda(\mathrm{Cu\,K}\alpha) = 1.54178$ Å, $T = 100$ K, $a = 4.9759(9)$ Å, $b = 17.655(3)$ Å, $c = 15.299(3)$ Å, $\beta = 97.809(9)°$, $V = 1331.6(4)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.458\ \mathrm{Mg/m^3}$, Anisotropic least-squares refinement (262 parameters/427 restraints) on 1873 independent merged reflections ($R_{\mathrm{int}} = 0.0955$), converged at $wR_2(F^2) = 0.2653$ for all data; $R_1(F) = 0.0939$ for 1165 observed data ($I > 2\sigma(I)$), GOF = 0.975. CCDC 250759 contains the supplementary crystallographic data for this paper.

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