Polycyclic Hydrocarbons

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Indeno[2,1-*b*]fluorene: A 20-π-Electron Hydrocarbon with Very Low-Energy Light Absorption**

*Akihiro Shimizu, Ryohei Kishi, Masayoshi Nakano, Daisuke Shiomi, Kazunobu Sato, Takeji Takui, Ichiro Hisaki, Mikiji Miyata, and Yoshito Tobe**

The study of low-energy light-absorbing molecules based on a topological alignment design for conjugated π electrons in organic molecules has attracted much interest in connection with functional dyes and materials for information storage.[1,2] There are two well-established design principles for low-energy light-absorbing hydrocarbons: 1) to extend the π-conjugation space for alternant hydrocarbons to reduce the energy gap between the frontier molecular orbitals (MOs), as in relatively small acenes[3] and rylenes[4] and 2) to feature non-alternant hydrocarbons such as azulenes[5,6] (Figure 1). Furthermore, large singlet biradical character contributes as well because of the small energy gap between the frontier MOs,[7–12] as in relatively large acenes,[9] biphenalenes,[10] anthenes,[11] and zethrenes[12] (Figure 1). As all of these molecules generally exhibit lower-energy light absorption with increasing π-conjugation space,[3,4,6,10–12] extension of these π-conjugation spaces leads to lower energy light absorption (Figure 1). In contrast, we herein report that an indeno[2,1-*b*]fluorene derivative, a non-alternant hydrocarbon with a moderate singlet biradical character, exhibits an extremely low-energy light absorption band whose absorption end extends to 2000 nm, despite its small conjugation space.

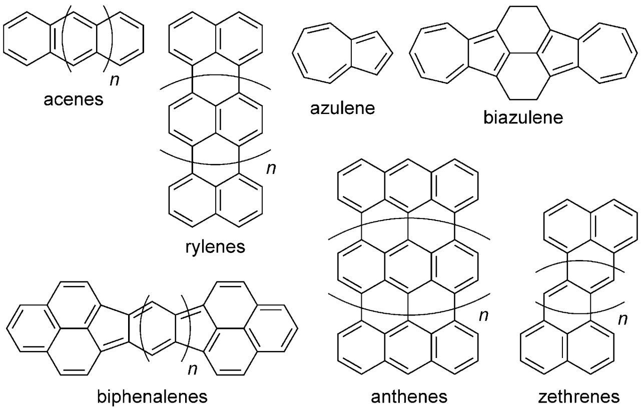

Figure 1. Representative hydrocarbons that exhibit low-energy light absorptions that decrease with increasing π-conjugation space.

We targeted indeno[2,1-*b*]fluorene (**1a**), because derivatives of its structural isomers, indeno[2,1-*a*]fluorene (**2a**),[13,14] indeno[1,2-*b*]fluorenes (**3a**),[15] and indeno[2,1-*c*]fluorene (**4a**)[16] have been intensively studied with respect to their unique optical properties, which are associated with their singlet biradical characters and low-energy band gaps (Figure 2). **1a** is expected to have a larger singlet biradical character than its isomers due to the *meta*-quinodimethane subunit, in contrast to the *ortho*- and *para*-quinodimethane structures. Indeed, theoretical calculations show that **1a** has a moderate singlet biradical character ($y = 0.68$ calculated by the Yamaguchi scheme[17] using the occupation numbers of the spin-unrestricted Hartree–Fock natural orbitals[18]), which is larger than that of **2a** ($y = 0.33$).[14] The spin density distribution for **1a** shows that the C10 and C12 carbons have the largest amplitudes (Figure 3). These results indicate that **1a** should be described as the resonance for the Kekulé and biradical structures (Figure 2a).

We synthesized 10,12-dimesitylindeno[2,1-*b*]fluorene (**1b**), wherein mesityl groups were introduced to stabilize the reactive sites through steric protection (Scheme 1). **1b** was obtained as a green solid in two steps by addition of mesitylmagnesium bromide to the known diketone **5**[19] followed by dehydroxylation of **6** with tin(II) chloride. In solution, **1b** gradually decomposes, in contrast to **2b**,[14] indicating that **1b** may have a larger singlet biradical

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[*] Dr. A. Shimizu,[+] Prof. Y. Tobe
Division of Frontier Materials Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama
Toyonaka, Osaka 560-8531 (Japan)
E-mail: tobe@chem.es.osaka-u.ac.jp

Dr. R. Kishi, Prof. M. Nakano
Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Osaka (Japan)

Dr. D. Shiomi, Prof. K. Sato, Prof. T. Takui
Department of Chemistry, Graduate School of Science, Osaka City University, Osaka (Japan)

Dr. I. Hisaki, Prof. M. Miyata
Department of Material and Life Science, Graduate School of Engineering, Osaka University, Osaka (Japan)

[+] Present address: Department of Synthetic and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto (Japan)

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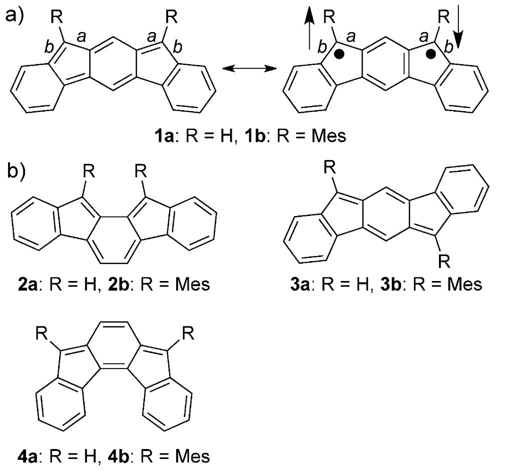


Figure 2. Structures of indenofluorenes **1**–**4**. a) Resonance structures of **1**. The arrows in the biradical structure represent antiparallel spins. b) Structures of **2**–**4**. Mes = 2,4,6-trimethylphenyl.

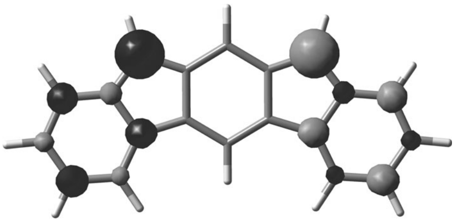
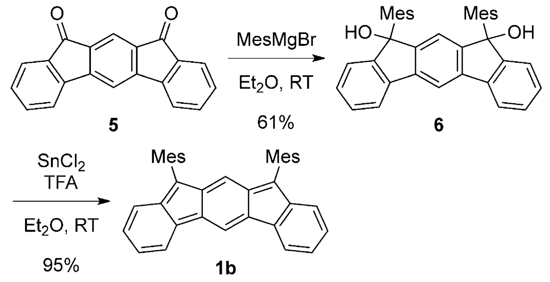


Figure 3. Spin density distribution of **1a** calculated at the UB3LYP/6-31G(d) level.



Scheme 1. Synthesis of **1b**. Mes = 2,4,6-trimethylphenyl, TFA = trifluoroacetic acid.

character. X-ray crystal structural analysis (Figure 4; see also the Supporting Information, Figure S3)[25] of **1b** provides crucial information on the singlet biradical character of **1b**, because the bond lengths reflect the contribution of the canonical structures.[20] The observed lengths for bonds *a* (1.437 Å) and *b* (1.431 Å) (Figure 2a for the bond positions), which agree with the theoretical values (Table S7), lie between the lengths of the C(sp^2)-C(sp^2) bond in benzene (1.39 Å) and the C(sp^2)-C(sp^3) bond in fluorene (1.468 Å).[21] This observation indicates that **1b** has a moderate contribution of the singlet biradical canonical structure to the ground-state electronic configuration.

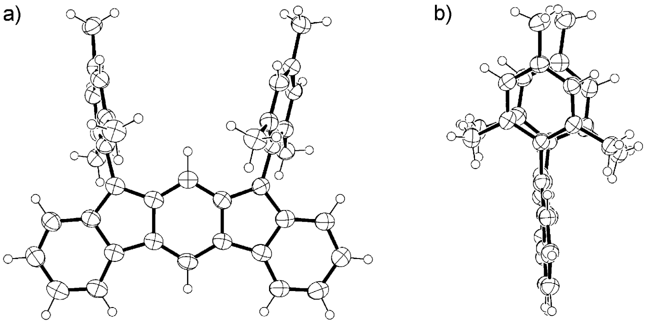


Figure 4. Crystal structure of **1b** (measured at 113 K). a) Top view. b) Side view. Displacement ellipsoids are drawn at the 50% probability level.

The small singlet–triplet energy gap in **1b**, which arises from the moderate singlet biradical character (y), was revealed experimentally. The temperature-dependent ^{1}H NMR spectra for **1b** showed no signal at +30 °C because of a thermally excited triplet species. However, after cooling to −93 °C, broad signals were observed (Figure 5). Although assignment was not possible owing to the broadness of the signals, they appeared at relatively high field (5.6–6.9 ppm). This is probably due to the antiaromatic character of the *s*-indacene moiety, as indicated by positive nucleus-independent chemical shift calculations (Table S8). Moreover, a triplet species for **1a** was observed by ESR spectroscopy (Figure S4a). With decreasing the temperature, the intensity of the ESR signal decreased, which indicates a singlet ground state in **1b** (Figure S4b). The singlet-triplet energy gap was estimated to be −2120 K (−17.6 kJ mol^{-1}) by temperature-dependent magnetic susceptibility measurements (Figure S5), which is reasonable for the $\Delta E_{S\text{-}T}$ for **1b**, which was theoretically estimated at −1240 K (−10.3 kJ mol^{-1}) at the UB3LYP/6-31G(d) level of theory. The stabilization of the singlet state of **1b** relative to the triplet state by the indenofluorene framework should be contrasted with

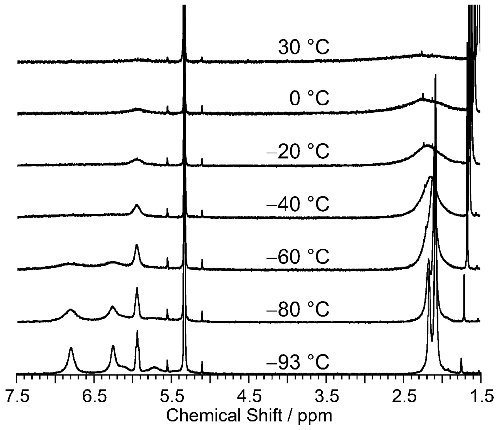


Figure 5. Temperature-dependent ^{1}H NMR spectra of **1b** in CD_2Cl_2. The peak at 5.3 ppm is due to $CDHCl_2$, and those at 5.55 and 5.1 ppm are due to its sidebands. Peaks at 1.55–1.75 ppm may be due to H_2O.

m-xylylene, the triplet ground state of which lies well below the singlet.[22] The small energy gap between the frontier MOs was supported by the energy difference between the first oxidation potential and the first reduction potential (E^{redox}) measured using cyclic voltammetry. The cyclic voltammogram for **1b** showed two reversible and two irreversible redox waves ($E_2^{\mathrm{ox,pa}} = +0.90$, $E_1^{\mathrm{ox}} = +0.13$, $E_1^{\mathrm{red}} = -1.13$, and $E_2^{\mathrm{red,pc}} = -2.03$ V vs. Fc/Fc$^+$; Figure S6). The measured E^{redox} value of 1.26 eV is consistent with the HOMO–LUMO energy gap (1.23 eV, HOMO: −4.37 eV, LUMO: −3.14 eV) calculated at the RB3LYP/6-31G(d)//UB3LYP/6-31G(d) level, and is less than the typical value for closed-shell hydrocarbons.

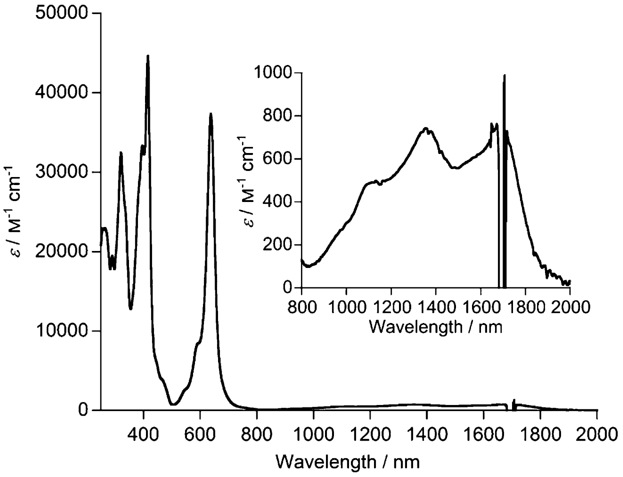
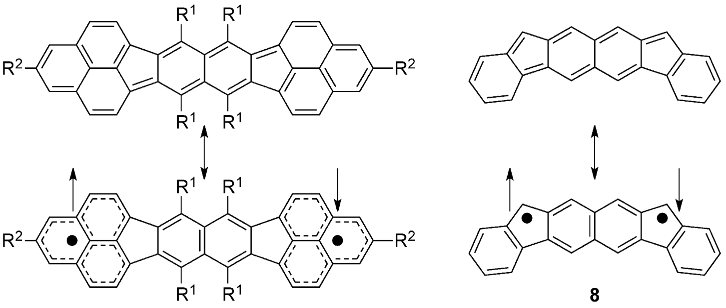


Figure 6. UV/Vis/NIR absorption spectrum of hydrocarbon **1b**. The spectrum was recorded in CH_2Cl_2 at room temperature. Inset shows a magnified view. The background absorbance at ca. 1700 nm may arise from the overtone of C−H vibration of the solvent.

The electronic absorption spectrum for **1b** in dichloromethane showed a strong absorption band at 638 nm and a weak absorption band at 850–2000 nm (Figure 6). Near-infrared absorption other than between singlet states may be observed because of 1) absorption contributed by impurities such as the **1b** radical cation, 2) intermolecular charge-transfer (CT) absorption, 3) singlet-to-triplet absorption, and 4) absorption of thermally excited triplet species. However, the following observations rule out these possibilities: 1) The time dependence of the electronic absorption spectrum showed that the lowest-energy band at 1700 nm diminished simultaneously with the band at 638 nm (Figure S7a). 2) The lowest-energy band with vibronic structures was independent of the concentration of **1a** (6.3×10^{-5} and 3.2×10^{-4} M; Figure S7b) and the solvent polarity (dichloromethane and acetonitrile; Figure S7c). 3) No external heavy-atom effect was observed in the iodoethane solution[23] (Figure S7c). 4) The extinction coefficient for the lowest-energy band was not dependent upon temperature (Figure S7d). Moreover, TD-DFT calculations at the TD-UB3LYP/6-31G(d) level predict S_0–S_1 absorption at 1232 nm for **1b** with a low oscillator strength ($f = 0.018$; Table S9), which is consistent with the experimental results. These results strongly suggest that the near-infrared band with a lowest-energy maximum at 1700 nm is from S_0–S_1 absorption in **1b**. The significant low-energy absorption band of **1b**, despite its small conjugation space, which consists of only 20 π electrons, should be contrasted with those of the known systems with similar number of π electrons, such as pentacene (22 π electrons, 578 nm),[3] perylene (20 π electrons, 439 nm),[4] and the biazulene shown in Figure 1 (20 π electrons, 633 nm),[6] as well as structural isomers **2b** (730 nm),[14] **3b** (516 nm),[15b] and **4b** (603 nm).[16]



7a : R1 = R2 = H, **7b** : R1 = Ph, R2 = *t*Bu

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Figure 7. Structures of biradicaloid compounds **7** and **8**. The arrows in the biradical structure represent antiparallel spins.

To demonstrate that the moderate amplitude of the biradical character of **1b** is critical for the exceptionally low-energy light absorption, we compared the lowest-energy transitions of **1a** (or **1b**) with those of the known biphenalene **7** and the hypothetical indenofluorene congener **8**, which have larger biradical characters (0.85 for **7a** and 0.79 for **8**), smaller HOMO–LUMO energy gaps (0.92 eV for **7a** and 1.08 eV for **8**), and larger π conjugation spaces (Figure 7). Experimentally, the absorption maxima of **1b** and **7b** are 1700 nm and 865 nm,[10b] respectively. Moreover, theoretical transitions estimated by TD-DFT calculations are 846 nm for **7a** and 985 nm for **8** (Tables S10 and S11). These results indicate that a molecule with a smaller π conjugation space exhibits a lower-energy light absorption if it has a moderate biradical character. We have revealed the theoretical background of this behavior on the basis of the valence configuration interaction scheme, which will be reported elsewhere.

In conclusion, the first example of *meta*-quinodimethane embedded in an indenofluorene framework is presented. We demonstrate that indeno[2,1-*b*]fluorene, which has a moderate singlet biradical character (*y*), exhibits extremely low-energy light absorption. We anticipate this knowledge is useful for the design of new classes of materials based on small molecules with low-energy light absorption.[24]

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[25] CCDC 884046 (**1b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.