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Highly fluorescent naphthacene derivatives and their photoconvertible precursors were synthesized for irreversibly photo-responsive fluorescent molecules. The fluorescence quantum yields (Φf) of the precursors were less than 0.02, and the precursors can be converted to the highly fluorescent naphthacene derivatives (Φf ≈ 0.67–0.70) quantitatively by photo-irradiation.

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Organic semiconducting molecules are very attractive for new device materials such as organic light emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaic cells (OPVCs). Acenes and their derivatives are classic fluorescent materials and can be used to fabricate OLEDs. In this context aryl-substituted acenes have been reported to improve the fluorescence quantum yields effectively. In many cases, however, these acenes are insoluble in common organic solvents due to their high crystallinity. To solve the problems, the soluble precursors with thermally or photochemically removable leaving groups have been synthesized. The photochemical conversion of an α-diketone precursor into anthracene with the production of two CO molecules has been known for a long time. This reaction has recently been applied to the photochemical synthesis of pentacene and larger acenes, which had been difficult to synthesize due to their air-instability and low solubility in common organic solvents. The methodology was also applied to the solution process to make OFET devices without using vacuum deposition.

Now we found this reaction is useful for the synthesis of highly fluorescent materials in situ from non-fluorescent compounds upon photoirradiation. Some photochromic molecules have been proposed for photo-responsive fluorescent molecules. However, in many cases these photochromic molecules undergo thermally or photochemically reversible reactions. As a result, the reacted molecules could be returned to the starting compounds. For the application to the bioimaging and read-only memories, an irreversible system is desirable. Herein we report the synthesis and spectroscopic properties of highly fluorescent naphthacene derivatives, 1b and 1c (Scheme 1), and their quantitative photochemical generation from their non-fluorescent α-diketone precursors (2a, 2b, and 2c), proposing irreversibly photo-responsive fluorescent molecules.

Scheme 1. Photochemical conversions of naphthacenediketones.

The synthesis of the substituted naphthacenes 1b and 1c is shown in Scheme 2. 1,1′-Biphenyl-4-ylidithium, which was prepared from 4-phenyl-bromobenzene and n-BuLi, was reacted with 5,12-naphthacenequinone (3) to afford 4b in 52% yield. The compound 4b was reacted with SnCl4 and conc. HCl in refluxing THF to give naphthacene 1b in 95% yield. Similarly 4c was prepared by the reaction of 3 and 3,5-diphenylphenyllithium, which was prepared from 1-iodo-3,5-diphenylbenzene in 29% yield, and then converted to 1c in 87%. The synthesis of α-diketone precursors 2a-c is also...
shown in Scheme 2. The Diels-Alder reaction of naphthacenes 1a-c with vinylene carbonate quantitatively gave 5a-c, respectively. Their hydrolysis followed by Swern oxidation gave α-diketone compounds 2a-c. The solubility of 1a, 1b, and 1c in toluene were respectively and their fluorescence lifetimes in benzene or diphenylnaphthacene and ruburene were respectively. Their hydrolysis followed by Swern oxidation of 1a, 2a, 2b, and 2c were much improved to 17, 15, and >23 mg/mL, respectively.

Absorption and fluorescence spectra of naphthacenes 1a-c in toluene are summarized in Figure 1 and Table 1. The absorption maxima of 1b and 1c in toluene were red-shifted by 20 nm in comparison with those of 1a. Fluorescence peaks of 1b (511 nm) and 1c (506 nm) are red-shifted by 30 and 25 nm from that of 1a (481 nm). The Stokes shifts of 1a-c are 6, 16, and 12 nm respectively, as shown in Table 1. The absolute fluorescence quantum yields of naphthacenes were 0.67 for 1a and 0.70 for 1c, which are more than 5 times larger than that of 1a (ΦF = 0.12). The fluorescence lifetimes (τF) of 1b and 1c were 9.4 and 9.6 ns, respectively, and are 2.5 times longer than that of 1a (τF = 3.9 ns) (Figure S1). These phenomena are similar to the relationship between naphthacene (1a), 5,12-diphenylnaphthacene, and 5,6,11,12-tetraphenylnaphthacene (ruburene). The ΦF’s of 1a, diphenylnaphthacene and ruburene were 0.12, 0.85, and 0.98, respectively, and their fluorescence lifetimes in benzene or toluene were reported as 4.2, 15.2, and 16 ns, respectively.14 The fluorescence spectra of 1a-c were also measured as shown in Figure S2. The quantum yields of 1a-c in solid state were <0.01, 0.03, and 0.11 respectively. The bulky substituents seemed to disturb the staking of the compounds in solid state.

The electrochemical properties of naphthacenes were investigated by cyclic voltammetry (CV) in anhydrous dichloromethane (Figure 2 and Table 1). One reversible oxidation peaks were observed for 1a (0.51 V vs. Fe/Fe⁺), 1b (0.44 V) and 1c (0.47 V), and the reduction potential observed for 1b (–2.10 V) and 1c (–2.09 V). The HOMO levels or ionization potentials (IP) were calculated by the known equation $IP = E_\text{ox} \pm 4.80$.15 The HOMO of 1b (5.17 eV) and 1c (5.20 eV) are lower than non-substituted naphthacene 1a by 0.06 and 0.03, respectively. The calculated HOMO energy levels relative to naphthacene 1a were also summarized in Table 1 (Figure S3).16

The UV-vis absorption spectra of α-diketone precursors 2a, 2b and 2c in toluene are shown in Figure 3. The absorption spectra show n-π* absorption of α-diketone moiety at 468 nm.
Table 1. Optical and electrochemical characterization of naphthacenes.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{on}$ [nm] (log $e$)</th>
<th>$\lambda_{on}$ [nm]</th>
<th>$\Phi_1$</th>
<th>$\tau_1$ [ns]</th>
<th>$E_{vis}^{on}$ [V$^{-1}$]</th>
<th>$E_{vis}^{on}$ [V$^{-1}$]</th>
<th>$E_{vis}^{on}$ [eV$^{-1}$]</th>
<th>$E_{vis}^{cal}$ [eV$^{-1}$]</th>
<th>LUMO$_{cal}$ [eV$^{-1}$]</th>
<th>LUMO$_{cal}$ [eV$^{-1}$]</th>
<th>$E_1$ [eV$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>396 (3.22), 419 (3.52), 445 (3.81), 475 (3.85)</td>
<td>481.512, 551</td>
<td>0.12</td>
<td>3.9</td>
<td>0.51</td>
<td>0.43</td>
<td>-</td>
<td>-5.23</td>
<td>-4.86</td>
<td>-2.66</td>
<td>-2.08</td>
</tr>
<tr>
<td>1b</td>
<td>411 (3.42), 436 (3.84), 463 (4.15), 495 (4.20)</td>
<td>511, 541, 583</td>
<td>0.67</td>
<td>9.4</td>
<td>0.44</td>
<td>0.37</td>
<td>-2.10</td>
<td>-5.17</td>
<td>-4.76</td>
<td>-2.75</td>
<td>-2.04</td>
</tr>
<tr>
<td>1c</td>
<td>464 (4.19), 494 (4.24)</td>
<td>506, 539, 589</td>
<td>0.70</td>
<td>9.6</td>
<td>0.47</td>
<td>0.40</td>
<td>-2.09</td>
<td>-5.20</td>
<td>-4.77</td>
<td>-2.77</td>
<td>-2.05</td>
</tr>
</tbody>
</table>

*aRecorded in toluene at room temperature.*

The absolute fluorescence quantum yield ($\Phi_1$) of 2a was not detected. The quantum yields of 2b and 2c were 0.016 and 0.017, respectively, in the beginning of the measurement, but $\Phi_1$'s were increased gradually at every measurement. These results imply that the precursors immediately reacted to release CO molecules when they were excited for the measurement of fluorescence quantum yield ($\lambda_{on}$ = 462 nm), and fluorescence from the generated acenes gradually observed depending on the irradiation period.

To investigate the photoreaction of the compounds 2a-c in detail, the photoreactions were monitored by $^1$H NMR spectroscopy (Figure 4). $\alpha$-Diketone precursor 2b was placed in degassed CDCl$_3$ and irradiated with blue LED ($\lambda$ = 470 nm, 25 W/m$^2$) under nitrogen atmosphere. During the photoreaction, the singlet peak of bridgehead protons at 5.2 ppm gradually decreased while singlet peak due to periposition of 1b increased at 8.4 ppm. These results suggested the photoreaction form 2b to 1b proceeded clearly. The photoconversion of $\alpha$-diketone precursor 2c to the naphthacene 1c gave the similar results (Figure S4).

Figure 4. $^1$H NMR spectra during the photoreaction of 2b in CDCl$_3$ under nitrogen atmosphere.

The change of UV-vis spectra during the photoreaction of 2b in toluene under argon atmosphere is shown in Figure 5a. Before irradiation, only the broad n-$\pi^*$ peak at 465 nm was observed. During the irradiation, the new peaks at 436, 463 and 495 nm assigned to 1b increased. The absorbance of naphthacene became constant after 60 min irradiation. Judging from the observation of the isosbestic point at 334 and 390 nm, the photoreaction proceeded directly. Similarly, $\alpha$-diketone precursors 2a and 2c were converted to 1a and 1c as shown in Figure S5. The change of the fluorescence spectra of 2b during the photoirradiation is shown in Figure 5b. The colorless fluorescence of the solution gradually changed to light green. Fluorescence intensity of 2b increases significantly with no change of the emission maxima position. After irradiation for 40 min, the fluorescence intensity stayed constant and the reaction seemed to be finished. The similar change was observed for 2c, as shown in Figure S6.

Figure 5. a) The UV-vis absorption spectra change of 2b upon photoirradiation in toluene (1.02 $\times$ 10$^{-7}$ M) under argon atmosphere ($\lambda_{on}$ = 468 nm). b) The fluorescence spectra change of 2b upon photoirradiation in toluene (3.48 $\times$ 10$^{-6}$ M) under argon atmosphere ($\lambda_{on}$ = 468 nm).

The photoconversion reaction was also performed in a PMMA film. PMMA (470 mg) was dissolved in toluene (10 mL), and the residue was filtered off after overnight stirring. The 150 $\mu$L of PMMA solution and 50 $\mu$L of CH$_2$Cl$_2$ solution of the precursor (5 mg/mL) were mixed. The mixture was spin-coated on glass plate and the film was irradiated for 1 h using a 375 W metal-halide lamp over 390 nm under vacuum. The experimental detail is described in the supporting information. The UV-vis spectra before and after photoirradiation are shown in Figure 6. Before irradiation, a typical n-$\pi^*$ absorption was observed at 470 nm. After irradiation, the peaks at 435, 463 and 494 nm appeared, similar to those in toluene solution. The fluorescence of 1b in the PMMA film was also observed which indicated the compound 2b was fully converted to 1b and the obtained acene compounds are dispersed in the PMMA film without stacking. The similar results were obtained for the photoconversion from 2c to 1c in PMMA film and the fluorescence quantum yields of 1b and 1c were 0.33 and 0.34, respectively, in the PMMA films.
In conclusions, we have succeeded in preparing the highly fluorescent naphthacenes 1b and 1c and their precursors 2b and 2c. The non-fluorescent precursors can be easily converted to highly fluorescent naphthacenes ($\Phi_f = 0.67-0.70$) by photo irradiation in solution. This conversion can be also possible in PMMA matrix. These new materials can be applicable in the field of OLED and memory media as printable fluorescent materials.

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Supporting Information Available Synthetic detail, characterization, fluorescence decay curves, and spectral change of absorption and fluorescence during the photolysis in solution are available.

References and Notes