Tetrahedron Letters 54 (2013) 1790–1793

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Photochemical synthesis of naphthacene and its derivatives for irreversible photo-responsive fluorescent molecules

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ARTICLE INFO

Article history:
Received 20 November 2012
Revised 28 December 2012
Accepted 7 January 2013
Available online 12 January 2013

Keywords:
Naphthacene
Photoconversion
Fluorescent
Photoprecursor

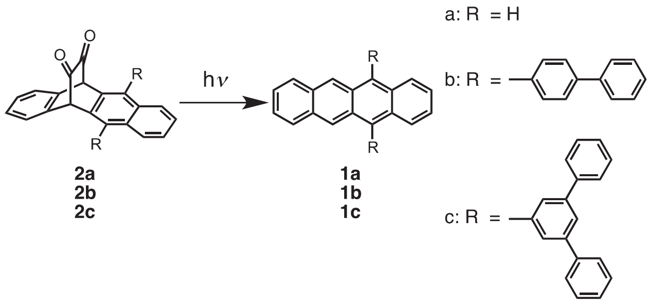
ABSTRACT

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

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.[1] In this context aryl-substituted acenes have been reported to improve the fluorescence quantum yields effectively.[2] In many cases, however, these acenes are insoluble in common organic solvents due to their high crystallinity. To solve such problems, the soluble precursors with thermally or photochemically removable leaving groups have been synthesized.[3–5] The photochemical conversion of an α-diketone precursor into anthracene with the production of two CO molecules has been known for a long time.[6] This reaction has recently been applied to the photochemical synthesis of pentacene and larger acences,[7,8] 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.[9]

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.[10,11] 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 of 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 (**2b**, and **2c**), proposing irreversibly photo-responsive fluorescent molecules.

The synthesis of the substituted naphthacenes **1b** and **1c** is shown in Scheme 2. 1,1′-Biphenyl-4-yllithium, which was prepared from 4-phenyl-bromobenzenene and *n*-BuLi, was reacted



Scheme 1. Photochemical conversions of naphthacenediketones.

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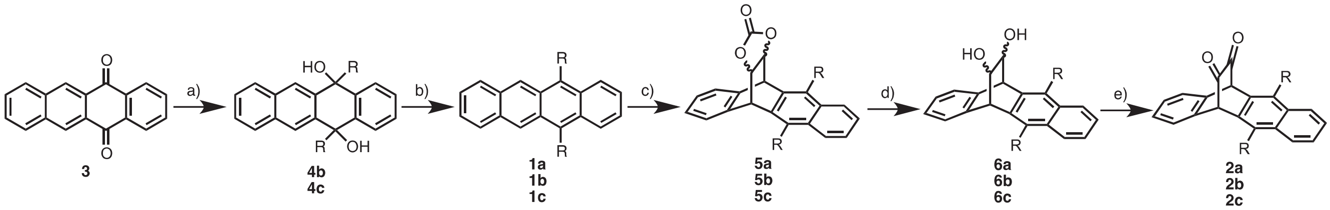
0040-4039/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2013.01.014



Scheme 2. Reagents and conditions: (a) 1,1′-biphenyl-4-yllithium for **4b** and 3,5-diphenylphenyllithium for **4c**, dry-toluene, dry-Et_2O, −45 °C, 5 h; **4b**: 52%; **4c**: 29%; (b) $SnCl_2$, concd HCl, reflux, 2 h; **1b**: 95%; **1c**: 87%; (c) vinylene carbonate, xylene, in autoclave, 180 °C, 3 days; **5a**: 95%; **5b**: 92%; **5c**: 78%; (d) 4 M NaOH aq, 1,4-dioxane, reflux, 2 h; **6a**: 95%; **6b**: 83%; **6c**: 72%; (e) dry-DMSO, TFAA, DIPEA, dry-CH_2Cl_2, −60 °C, 1.5 h; **2a**: 69%; **2b**: 85%; **2c**; 82%.

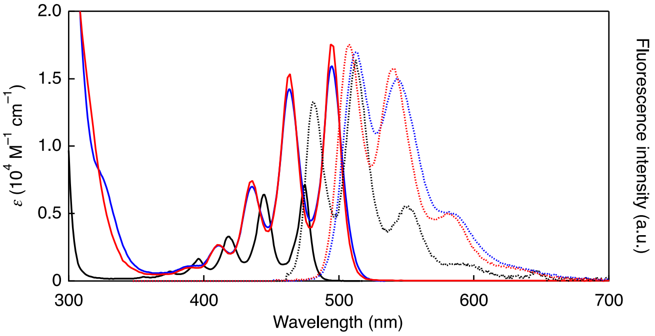


Figure 1. Absorption spectra (solid lines) and fluorescence spectra (dotted lines) of **1a** (black), **1b** (blue), and **1c** (red) in toluene.

with 5,12-naphthacenequinone (**3**) to afford **4b** in 52% yield. The compound **4b** was reacted with $SnCl_2$ and concd 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,[12,13] in 29% yield, and then converted to **1c** in 87% yield. 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 0.15, 0.81, and 5.2 mg/mL, respectively, and the solubility of the precursors **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 **1b** and 0.70 for **1c**, which are more than 5 times larger than that of **1a** (Φ_f = 0.12). The fluorescence lifetimes (τ_f) of **1b** and **1c** were 9.4 and 9.6 ns, respectively, and are 2.5 times longer than that of **1a** (τ_f = 3.9 ns) (Fig. S1). These phenomena are similar to the relationship between naphthacene (**1a**), 5,12-diphenylnaphthacene, and 5,6,11,12-tetraphenylnaphthacene (ruburene). The Φ_f'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 stacking of the compounds in solid state.

The electrochemical properties of naphthacenes were investigated by cyclic voltammetry (CV) in anhydrous dichloromethane (Fig. 2 and Table 1). Reversible oxidation peaks were observed for **1a** (0.51 V vs Fc/Fc^+), **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^{ox}_{onset} +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** are also summarized in Table 1 (Fig. 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.

The absolute fluorescence quantum yield (Φ_f) of **2a** was not detected. The Φ_f of **2b** and **2c** were 0.016 and 0.017, respectively, in the beginning of the measurement, but Φ_f'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 (λ_{ex} = 462 nm), and fluorescence from the generated acenes were 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 (Fig. 4). α-Diketone precursor **2b** was placed in degassed $CDCl_3$ and irradiated with blue LED (λ = 470 nm, 25 W/m^2) under nitrogen atmosphere. During the photoreaction, the singlet peak of

Table 1
Optical and electrochemical characterization of naphthacenes

	λ_{abs}[a] (nm) (log ε)	λ_{em}[a] (nm)	Φ_f	τ_f (ns)	$E^{ox}_{1/2}$ (V)[b]	E^{ox}_{onset} (V)[b]	$E^{red}_{1/2}$ (V)[b]	$HOMO_{exp}$ (eV)[c]	$HOMO_{cal}$ (eV)[d]	$LUMO_{exp}$ (eV)[e]	$LUMO_{cal}$ (eV)[d]	E_g (eV)[f]
1a	396 (3.22), 419 (3.52), 445 (3.81), 475 (3.85)	481, 512, 551	0.12	3.9	0.51	0.43	—	−5.23	−4.86	−2.66[f]	−2.08	2.57
1b	411 (3.42), 436 (3.84), 463 (4.15), 495 (4.20)	511, 541, 583	0.67	9.4	0.44	0.37	−2.10	−5.17	−4.76	−2.75	−2.04	2.42
1c	410 (3.43), 436 (3.87), 464 (4.19), 494 (4.24)	506, 539, 589	0.70	9.6	0.47	0.40	−2.09	−5.20	−4.77	−2.77	−2.05	2.43

[a] Recorded in toluene at room temperature.
[b] The values were obtained by cyclic voltammetry. V versus Fc/Fc^+. See Supplementary data for experimental details.
[c] The values were obtained by ionization potentials in toluene.
[d] The values were calculated at the B3LYP/6-31G(d) levels.
[e] The values were obtained from HOMO levels and E_g.
[f] The values were obtained from the edge of the absorption spectra in toluene.

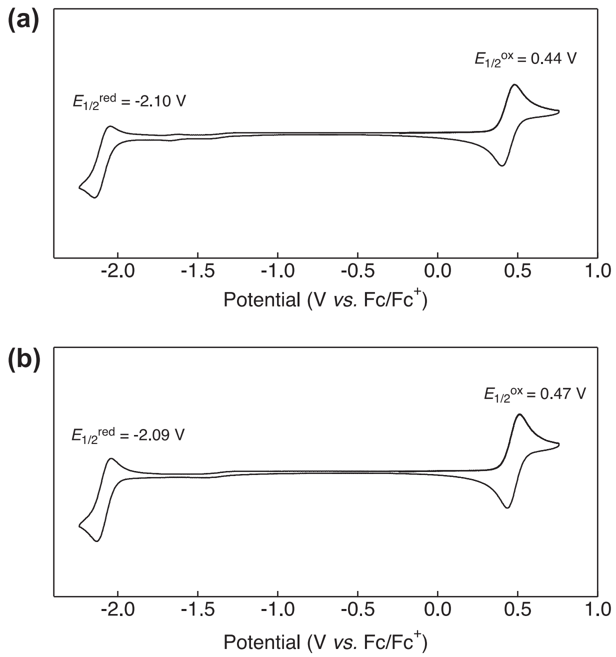


Figure 2. Cyclic voltammograms of **1b** (a) and **1c**; (b) in 0.1 M TBAPF$_6$ in acetonitrile. Scan rate 0.1 V/s. [Naphthacene] = 0.1 mM. WE: glassy carbon, CE: Pt, RE: Ag/AgNO$_3$.

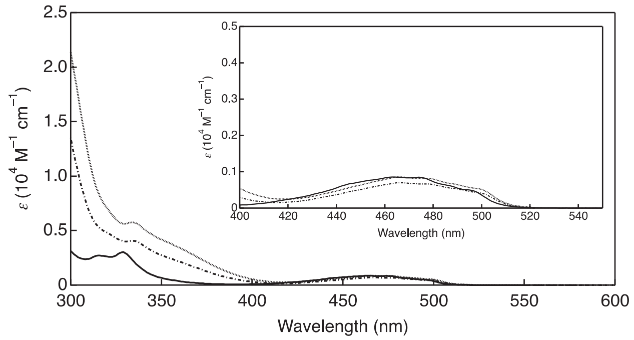


Figure 3. Absorption spectra of α-diketone **2a** (black line), **2b** (gray line), **2c** (dotted line).

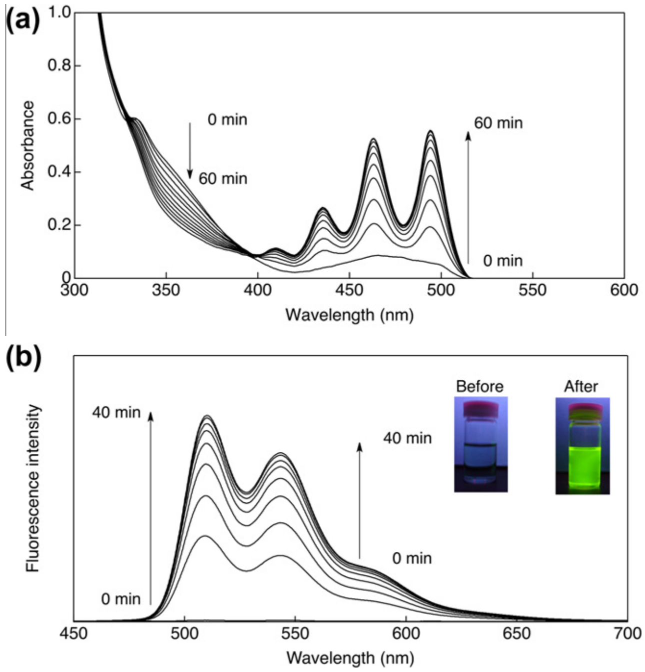


Figure 5. (a) The UV–vis absorption spectra change of **2b** upon photoirradiation in toluene (1.02×10^{-4} M) under argon atmosphere (λ_{ex} = 468 nm); (b) the fluorescence spectra change of **2b** upon photoirradiation in toluene (3.48×10^{-5} M) under argon atmosphere (λ_{ex} = 468 nm).

bridgehead protons at 5.2 ppm gradually decreased while singlet peak due to peri-position of **1b** increased at 8.4 ppm. These results suggested the photoreaction form **2b** to **1b** proceeded clearly. The photoconversion of α-diketone precursor **2c** to the naphthacene **1c** gave similar results (Fig. S4).

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–π* 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 points at 334 and 390 nm, the photoreaction proceeded directly. Similarly, α-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.

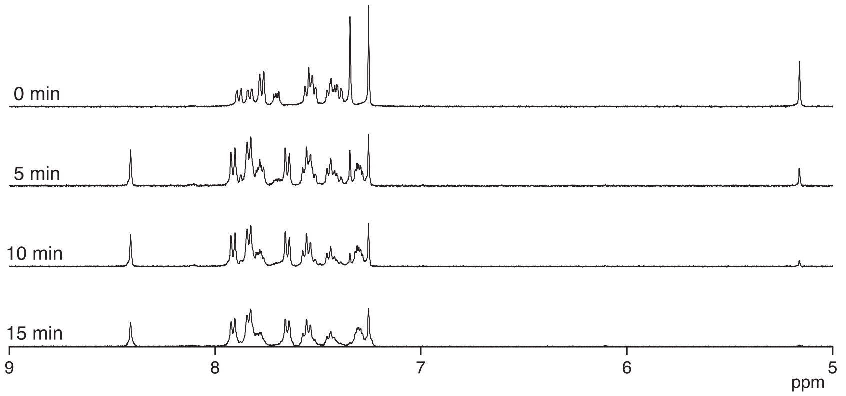


Figure 4. ^{1}H NMR spectra during the photoreaction of **2b** in CDCl$_3$ under nitrogen atmosphere.

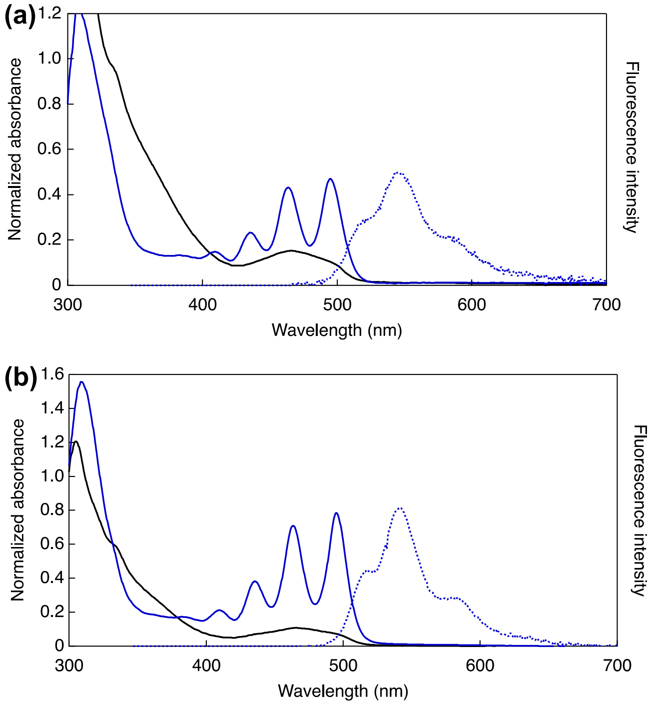


Figure 6. UV–vis absorption (solid lines) and fluorescence (dotted lines) spectra of (a) **1b** (blue) and **2b** (black); and (b) **1c** (blue) and **2c** (black) in PMMA films (λ_{ex} = 435 nm).

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. 150 μL of PMMA solution and 50 μL of CH_2Cl_2 solution of the precursor (5 mg/mL) were mixed. The mixture was spin-coated on a 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 Supplementary data. The UV–vis spectra before and after photoirradiation are shown in Figure 6. Before irradiation, a typical n–π^* 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. 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 (Φ_f = 0.67–0.70) by photo irradiation in solution. This conversion can also be possible in PMMA matrix. These new materials can be applicable in the field of OLED and memory media as printable fluorescent materials.

Acknowledgments

We thank Division of Synthesis and Analysis, Department of Molecular Science, Integrated Center for Sciences (INCS), Ehime University for its help in using mass and NMR spectrometer. We also thank Venture Business Laboratory, Ehime University, for its help in using TOF-MS. This work was partially supported by Grants-in-Aid (No. 22350083 to H.Y.) and the Green Photonics Project in NAIST sponsored by the Ministry of Education, Culture, Sports, Science and Technology, MEXT, Japan, and Adaptable and Seamless Technology Transfer Program through Target-driven R&D (A-STEP) (No. AS2111283D to S.F. and H.Y.) sponsored by Japan Science and Technology Agency.

Supplementary data

Supplementary data (synthetic detail, characterization, fluorescence decay curves, and spectral change of absorption and fluorescence during the photolysis in solution) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.01.014.

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