

# In Situ Preparation of Highly Fluorescent Pyrene-Dyes from Non-luminous Precursors Upon Photoirradiation

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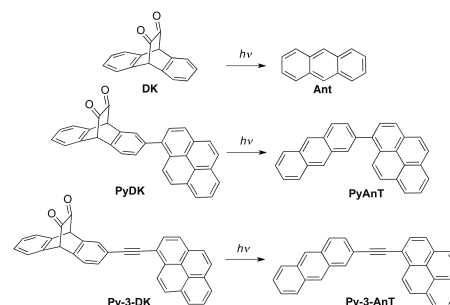
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Non-luminous precursor, 2-(1-pyrenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dione, was photochemically converted to highly-fluorescent 2-(1-pyrenyl)anthracene quantitatively in solution and in PMMA film and the fluorescence quantum yield of the acene in benzonitrile was as high as 0.99.

Fluorescent molecular probes are of great interest due to their versatile applications in chemical, environmental and biological science. Fluorescence is one of the most promising tools for the detection of small amounts of molecules, since fluorescence can even be detected in only one molecule and is applied in various areas such as microanalysis,<sup>1</sup> bioimaging<sup>2</sup> and memory media.<sup>3</sup> Recently an efficient conversion of non-luminous molecules to highly-fluorescent molecules by external stimuli like heat or light have received attention due to their potential for the application in optical memory media, fluorescence imaging and super-resolution fluorescence imaging.<sup>4-10</sup> In this context, one-way conversion would be desirable for read-only memory and single-molecule microscopy.

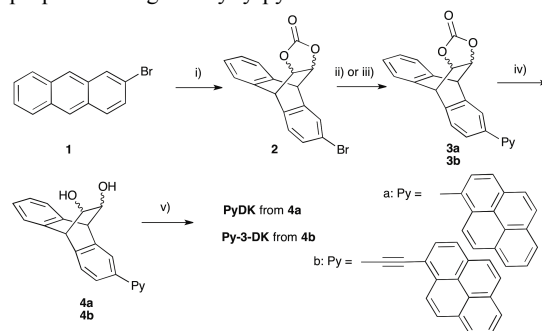
Pyrene is a versatile blue-fluorophore with high fluorescence quantum yields. Aryl-pyrene compounds are one of the highly fluorescent materials,<sup>11</sup> but unfortunately their solubility in common organic solvent is quite low and the purification is difficult. In this regard a photochemical quantitative conversion of 9,10-dihydro-9,10-ethanoanthracene-11,12-dione (DK) to anthracene (Ant) is an useful one-way reaction in solution or film (Scheme 1)<sup>12</sup>. This reaction has recently been applied to the photochemical synthesis of pentacene<sup>13</sup> and its relatives for the fabrication of FET devices by a solution process<sup>14</sup>, and for the protecting groups to prepare air-unstable substituted pentacenes<sup>15</sup> and larger acenes<sup>16</sup>. Furthermore we found the diketone moieties can work as an intramolecular quencher of the fluorophore for the substituted tetracene compounds, resulting the in-situ photochemical conversion from a non-fluorescent precursor to a fluorescent compound.<sup>17</sup> In connection with these results, this photoconversion will be ideal for the synthesis of highly pure and highly fluorescent aryl-pyrene compounds from soluble and non-luminous precursors. We report here an in situ quantitative preparation of highly blue-fluorescent pyrene-anthracene dyes (PyAnt and Py-3-Ant) from non-luminous  $\alpha$ -diketone precursors (PyDK and Py-3-DK) upon photoirradiation in solution and in film (Scheme 1).

PyAnt can be prepared by Suzuki-Miyaura coupling of 2-bromoanthracene (1) and pyreneboronic acid, however the



Scheme 1. Photoconversion from  $\alpha$ -diketone to pyrenylanthracenes.

yield was only 3 % due to its low solubility. Py-3-Ant can be also prepared by Sonogashira coupling from 1 and 1-ethynylpyrene in 12%, but the purification on silica gel column chromatography was difficult because of the low solubility and close  $R_f$  values with byproducts. To solve the solubility problem, the precursors PyDK and Py-3-DK were prepared as shown in Scheme 2. 2-Bromoanthracene 1 was reacted with vinylene carbonate by Diels-Alder reaction to give adduct 2 in 76% yield. The compound 2 was coupled with pyreneboronic acid by Suzuki-Miyaura coupling to give adduct 3a in 51% yield. The obtained adduct 3a was hydrolyzed to give diol compound 4a in 74% yield, followed by Swern oxidation to give PyDK in 14% yield. Py-3-DK was also prepared using 2-ethynylpyrene as shown in Scheme 2.

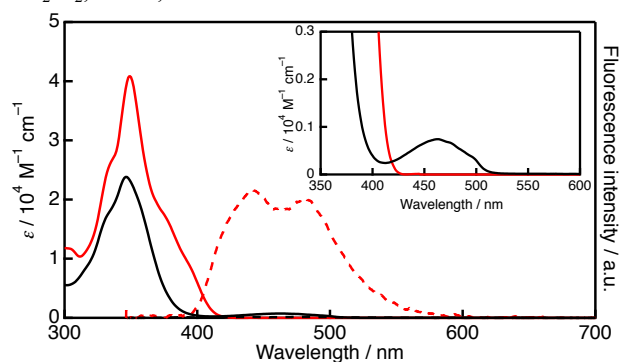


Reagents and conditions: i) vinylene carbonate, xylene, autoclave, 180 °C, 3 d, 76%; ii) for 3a, pyreneboronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, 1,4-dioxane, reflux, 18 h, 51%; iii) for 3b, 2-ethynylpyrene, CuI, Et<sub>3</sub>N, Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene, reflux, 18 h, 34%; iv) K<sub>2</sub>CO<sub>3</sub>, THF, methanol, H<sub>2</sub>O, rt, overnight, 74% for 4a and 61% for 4b; v) TFAA, dry-DMSO, *N,N*-(*iso*-pro)<sub>2</sub>EtN, dry-CH<sub>2</sub>Cl<sub>2</sub>, 1.5 h, 14% for PyDK and 60% for Py-3-DK.

Scheme 2. Syntheses of PyDK and Py-3-DK.

The UV-vis absorption and fluorescence spectra of PyAnt and PyDK in toluene are shown in Figure 1. PyAnt has an

absorption peak at 349 nm ( $\epsilon = 4.50 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ) with shoulders at both sides in toluene. The emission peaks were observed at 443 and 478 nm with the fluorescence quantum yield ( $\Phi_f$ ) of 0.86 in toluene. The fluorescence peak (443 nm) of **PyAnt** showed red-shift by 68 nm from parent pyrene due to the through-bond interaction between pyrene and anthracene moieties. The absorption spectra were similar in toluene,  $\text{CH}_2\text{Cl}_2$ , benzonitrile, and DMSO, but the fluorescence of **PyAnt** showed solvatochromic shift as shown in Table 1 and ESI†, Figure S1. The fluorescence peaks ( $\lambda_{em}$ ) gave bathochromic shifts by increasing the polarity of the solvents:  $\lambda_{em} = 443 \text{ nm}$  ( $\Phi_f = 0.86$ ) in toluene, 486 nm (0.92) in  $\text{CH}_2\text{Cl}_2$ , 486 nm (0.99) in PhCN, and 496 nm (0.91) in DMSO. These results are well coincident with the known superposition of a nonpolar locally excited (LE) and a strongly polar charge transfer (CT) contribution of substituted pyrene compounds.<sup>11</sup> The fluorescence lifetimes ( $\tau_f$ ) were also measured (Table 1 and ESI†, Figure S2). Since the rotary motion around the C-C linkage between pyrene and anthracene is possible, **PyAnt** showed bi-exponential decay in  $\text{CH}_2\text{Cl}_2$ , PhCN, and DMSO.



**Figure 1.** The absorption (solid lines) and fluorescence (dashed lines) spectra of **PyDK** (black) and **PyAnt** (red) in toluene; excited at 380 nm.

**PyDK** has the peak of pyrene moiety at 348 nm ( $\epsilon = 2.71 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ) in toluene and the absorption of diketone moiety at 461 nm ( $\epsilon = 7.40 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$ ). The absorption at 461 nm is similar with the absorption of non-substituted **DK** (ESI†, Figure S3) but absorption of **PyDK** at 461 nm is slightly larger than that of **DK** due to the overlap of CT-like absorption from pyrene moiety to carbonyl moiety, as predicted by TD-DFT calculation (ESI†, Figures S4). **PyDK** was non-fluorescent with excitation at 380 and 460 nm due

to the quenching of the excited state of pyrene by diketone moiety (Figure 1 and ESI†, Figure S5).

The similar tendency was observed for **Py-3-Ant** and **Py-3-DK**. UV-vis absorption spectrum of **Py-3-Ant** showed four peaks at 308, 365, 393 and 418 nm in toluene (ESI†, Figures S3 and S6). Due to the triple bonds between pyrene and anthracene moieties, the  $\pi$ -conjugation of **Py-3-Ant** expanded more than that of **PyAnt**, which gave the red-shift of the absorption spectra. Fluorescence spectra of **Py-3-Ant** also showed the solvent effects:  $\lambda_{em} = 426, 450$  and  $482 \text{ nm}$  in toluene ( $\Phi_f = 0.90$ );  $485 \text{ nm}$  in  $\text{CH}_2\text{Cl}_2$  (0.92);  $488 \text{ nm}$  (0.94) in PhCN;  $497 \text{ nm}$  (0.95) in DMSO. The fluorescence lifetimes ( $\tau_f$ ) were also measured (Table 1 and ESI†, Figure S7). **Py-3-Ant** showed single-exponential decays due to the rigid linkage with a triple bond.

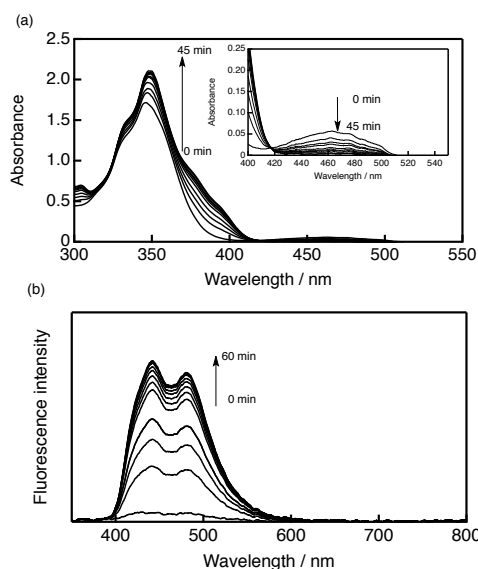
To investigate the photocleavage reaction of **PyDK**, the photoconversion was monitored by  $^1\text{H}$  NMR spectroscopy under an argon atmosphere (ESI†, Figure S8). **PyDK** was placed in degassed  $\text{CDCl}_3$  and irradiated at  $470 \text{ nm}$  with a xenon light source through monochromator ( $14.9 \text{ mW/cm}^2$ ). During the photoconversion, the singlet peaks at 5.1 and 5.2 ppm due to bridge-head protons of **PyDK** gradually decreased while peaks of peri-positions of **PyAnt** increased at 8.5 ppm. After 25 min the photoconversion finished without giving any by-products. The  $^1\text{H}$  NMR spectrum at 25 min was identical with the spectrum of **PyAnt**, directly prepared by Suzuki-Miyaura coupling of **1** and pyreneboronic acid. The photoreaction of **Py-3-DK** to **Py-3-Ant** also proceeded successfully (ESI†, Figure S8).

The change in UV-vis absorption spectra during the photolysis of **PyDK** was monitored. When **PyDK** was irradiated at  $468 \text{ nm}$  ( $1.86 \text{ mW/cm}^2$ ), the decarbonylation occurred giving the corresponding **PyAnt** (ESI†, Figure S9). The relative quantum yield of the photoconversion reaction of **PyDK** excited at  $468 \text{ nm}$  was 0.29, compared to the absolute quantum yield of **DK** (0.37). The photoreactions of **PyDK** was also performed by excitation at  $\pi$ - $\pi^*$  absorption of pyrene moieties ( $370 \text{ nm}$ ,  $< 0.88 \text{ mW/cm}^2$ ), monitored by the spectra change of the absorption and fluorescence in toluene (Figures 2). During the irradiation, the blue fluorescence increased, since **PyDK** was not fluorescent while **PyAnt** was strongly fluorescent. The same phenomenon was also observed for **Py-3-DK** and **Py-3-Ant** and the relative quantum yield of the photoconversion reaction of **Py-3-DK** was 0.27 (ESI†, Figure S9 and S10).

**Table 1** Absorption and fluorescence peaks ( $\lambda_{abs}$  and  $\lambda_{flu}$ ), fluorescence quantum yields ( $\Phi_f$ ), and fluorescence lifetimes ( $\tau_f$ ) of **PyAnt** and **Py-3-Ant** in various solvents<sup>a</sup>.

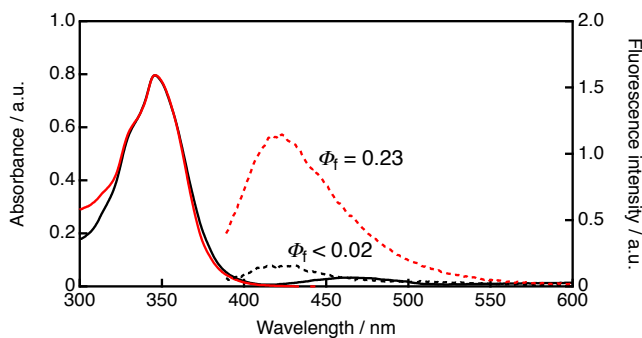
Compounds	Solvents	$\lambda_{abs} / \text{nm}$	$\lambda_{flu} / \text{nm}^a$	$\Phi_f^b$	$\tau_f / \text{ns} (\text{A})^c$	$\chi^2$	
<b>PyAnt</b>	Toluene	2.38	349	443, 478	0.86	4.22	1.64
	$\text{CH}_2\text{Cl}_2$	8.93	348	486	0.92	4.26 (0.46) 6.71 (0.54)	1.33
	PhCN	25.2	352	486	0.99	4.79 (0.85) 8.78 (0.15)	1.39
	DMSO	46.5	351	496	0.91	4.47 (0.61) 7.69 (0.39)	1.11
	<b>Py-3-Ant</b>	Toluene	2.38	308, 365, 393, 418	426, 450, 482	0.90	1.98 (0.99) 6.74 (0.01)
$\text{CH}_2\text{Cl}_2$	8.93	306, 364, 391, 416	485	0.92	2.85	1.52	
PhCN	25.2	310, 366, 397, 420	488	0.94	2.96	1.14	
DMSO	46.5	308, 367, 397, 421	497	0.95	3.56 (0.92) 5.59 (0.08)	1.40	

<sup>a</sup> dielectric constant; <sup>b</sup>  $\lambda_{flu}$  and  $\Phi_f$  were measured by excitation at 380 nm. <sup>c</sup>  $\tau_f$  was measured by excitation at 366 nm.



**Figure 2.** (a) The change in (a) absorption spectra ( $5.6 \times 10^{-5}$  M) and (b) fluorescence spectra ( $4.4 \times 10^{-5}$  M) during photolysis ( $\lambda_{\text{ex}} = 370$  nm) of **PyDK** in toluene.

Finally we have performed the photoconversion of **PyDK** and **Pt-3-DK** in PMMA film, as shown in Figure 3 and ESI†, Figure S11. After the photoirradiation over >390 nm for 10 min, the  $\Phi_f$  of **Py-Ant** was increased to 0.23. For the **PyDK** film fluorescence was also observed around 420 nm with  $\Phi_f$  less than 0.02, which belonged to **Py-Ant** generated during the measurement. This result indicates **PyDK** in film is highly sensitive to the light and the photoconversion from **PyDK** to **Py-Ant** occurred during the measurement. The  $\Phi_f$  of PMMA film of **Py-3-Ant** prepared by this photoconversion was 0.11.



**Figure 3.** Absorption and emission spectra of **PyDK** (black) and **PyAnt** (red) in PMMA film; excited at 380 nm.

## Conclusions

We have succeeded in preparing the **PyDK** and **Py-3-DK** as latent fluorophores which can be effectively converted to highly blue-fluorescent **PyAnt** and **Py-3-Ant** by photoirradiation in solution and in film. The one-way convertible precursors of highly-fluorescent fluorophores will be promising for the various applications in the areas of microanalysis and memory media.

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## Notes and references

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- † Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/
- ‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
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