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In Situ Preparation of Highly Fluorescent Pyrene-Dyes from Nonluminous Precursors Upon Photoirradiation

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Non-luminous precursor, 2-(1-pyrenyl)-9,10-dihydro-9,10ethanoanthracene-11,12-dione, was photochemically converted to 10 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 ¹⁵ 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, ¹ bioimaging² and memory media.³ Recently an efficient conversion of non-²⁰ 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.⁴⁻¹⁰ In this context, one-way conversion would be

- imaging.⁴⁻¹⁰ In this context, one-way conversion would be ²⁵ 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 fluorecent materials,¹¹ but unfortunately their solubility in ³⁰ 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-11,12dione (**DK**) to anthracene (**Ant**) is an useful one-way reaction in solution or film (Scheme 1)¹². This reaction has recently ³⁵ been applied to the photochemical synthesis of pentacene¹³
- and its relatives for the fabrication of FET devices by a solution process¹⁴, and for the protecting groups to prepare air-unstable substituted pentacenes¹⁵ and larger acenes¹⁶. Furthermore we found the diketome moities can work as an
- ⁴⁰ intramolecular quncher of the fluorophore for the substited tetracene compounds, resulting the in-situ photochemical conversion from a non-fluorescent precursor to a fluorescent compound.¹⁷ In connection with these results, this photoconversion will be ideal for the synthesis of highly pure
- ⁴⁵ and highly fluorescent aryl-pyrene compounds from soluble and non-luminous precursors. We report here an in situ quantitative preparation of highly blue-fluorescent pyreneanthracene dyes (**PyAnt** and **Py-3-Ant**) from non-luminous αdiketone precursors (**PyDK** and **Py-3-DK**) upon ⁵⁰ photoirradiation in solution and in film (Scheme 1).
- **PyAnt** can be prepared by Suzuki-Miyaura coupling of 2bromoanthracene (1) and pyreneboronic acid, however the



Scheme 1. Photoconversion from α -diketone to pyrenylanthracenes.

⁵⁵ yield was only 3 % due to its low solubility. **Py-3-Ant** can be also prepared by Sonogashira couplung 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 ⁶⁰ 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 ⁶⁵ 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.



70 Reagents and conditions: i) vinylene carbonate, xylene, autoclave, 180 °C, 3 d, 76%; ii) for **3a**, pyreneboronic acid, Pd(PPh₃)₄, Na₂CO₃, 1,4-dioxane, reflux, 18 h, 51%; iii) for **3b**, 2-ethynylpyrene, CuI, Et₃N, Pd(PPh₃)₄, toluene, reflux, 18 h, 34%; iv) K₂CO₃, THF, methanol, H₂O, rt, overnight, 74% for **4a** and 61% for **4b**; v) TFAA, 75 dry-DMSO, N,N-(iso-pro)₂EtN, dry-CH₂Cl₂, 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 ($\varepsilon = 4.50 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$) with shoulders at both sides in toluene. The emission peaks were observed at 443 and 478 nm with the fluorecence quantum vield ($\Phi_{\rm f}$) of 0.86 in toluene. The fluorescence peak (443 nm) 5 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, CH₂Cl₂, benzonitrile, and DMSO, but the fluorescence of PyAnt showed solvatochromic shift as shown ¹⁰ in Table 1 and ESI⁺, Figure S1. The fluorescnece peaks (λ_{em}) gave bathochromic shifts by increasing the polarity of the solvents: $\lambda_{em} = 443$ nm ($\Phi_f = 0.86$) in tolunene, 486 nm (0.92) in CH₂Cl₂, 486 nm (0.99) in PhCN, and 496 nm (0.91) in DMSO. These result are well coincident with the known 15 superposition of a nonpolar locally excited (LE) and a strongly polar charge transfer (CT) contribution of substituted pyrene compounds.¹¹ The fluorescence lifetimes ($\tau_{\rm f}$) were also measured (Table 1 and ESI⁺, Figure S2). Since the rotary motion around the C-C linkage between pyrene and 20 anthracene is possible, PyAnt showed bi-exponential decay in CH₂Cl₂, 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.

²⁵ **PyDK** has the peak of pyrene moiety at 348 nm ($\varepsilon = 2.71 \times 10^4 \,\mathrm{M}^{-1} \mathrm{cm}^{-1}$) in toluene and the absorption of diketone moiety at 461 nm ($\varepsilon = 7.40 \times 10^2 \,\mathrm{M}^{-1} \mathrm{cm}^{-1}$). 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 ³⁰ larger than that of **DK** due to the overlap of CT-like absorption from pyrene moiety to carbonyl moiety, as predicted by TD-DFT calcuration (ESI[†], Figures S4). **PyDK** was non-fluoresocent with excitation at 380 and 460 nm due

to the quenching of the excited state of pyrrene by diketone ³⁵ moiety (Figure 1 and ESI[†], Figure S5).

The similar tendancy 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 ⁴⁰ anthracene moieties, the π -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 nm in toluene ($\Phi_f = 0.90$); 485 nm in CH₂Cl₂ (0.92); 488 nm (0.94) ⁴⁵ in PhCN: 497 nm (0.95) in DMSO. The fluorescence lifetimes

 $(\tau_{\rm f})$ 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 ⁵⁰ photoconversion was monitored by ¹H NMR spectroscopy under an argon atmosphere (ESI[†], Figure S8). **PyDK** was placed in degassed CDCl₃ and irradiated at 470 nm with a xenon light source through monochromater (14.9 mW/cm²). During the photoconversion, the singlet peaks at 5.1 and 5.2

⁵⁵ 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 ¹H NMR spectrum at 25 min was identical with the spectrum of **PyAnt**, directly prepared by Suzuki-⁶⁰ 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 65 irradiated at 468 nm (1.86 mW/cm²), the decarbonylation occurred giving the corresponding PyAnt (ESI⁺, Figure S9). The relative quantum yield of the photoconversion reaction of **PyDK** excited at 468 nm was 0.29, compared to the absolute quantum yield of DK (0.37). The photoreactions of PyDK ⁷⁰ was also performed by excitation at π - π * absorption of pyrene moieties (370 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 75 fluorescent. The same phenomenum was also observed for Py-3-DK and Pv-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 (λ_{abs} and λ_{flu}), fluorescence quantum yields (\mathcal{O}_{f}), and fluorescence lifetimes (τ_{f}) of **PyAnt** and **Py-3-Ant** in various solvents^a.

Compounds	Solvents		$\lambda_{ m abs}$ /nm	$\lambda_{\mathrm{flu}}/\mathrm{nm}^{\mathrm{a}}$	$arPsi_{ m f}^{ m b}$	$ au_{ m f}$ /ns (A) ^c	χ^2
PyAnt	Toluene	2.38	349	443, 478	0.86	4.22	1.64
-	CH_2Cl_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
Py-3-Ant	Toluene	2.38	308, 365, 393, 418	426, 450, 482	0.90	1.98 (0.99) 6.74 (0.01)	1.68
-	CH_2Cl_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

^a dielectric constant; ${}^{b}\lambda_{flu}$ and Φ_{f} were measured by excitation at 380 nm. ${}^{c}\tau_{f}$ was measured by excitation at 366 nm.

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

⁵ 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 Φ_f of **Py-Ant** was incressed to 0.23. For the **PyDK** film fluorecence was also observed around 420 nm with Φ_f ¹⁰ 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 Φ_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

- ²⁰ 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 soliution and in film. The one-way convertible precursors of highly-fluorescent fluorophores will ²⁵ be promising for the various applications in the areas of ²⁶
- microanalysis and memory media.

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