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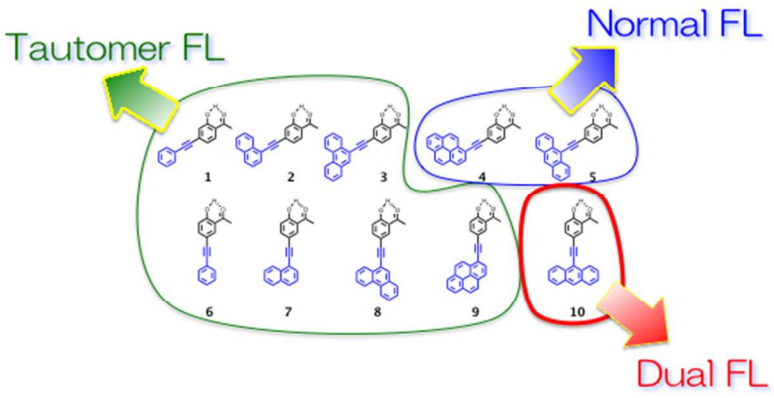

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Targetting production of a dual-fluorescent molecule by tuning the energetics of excited-state intramolecular proton transfer

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We report herein the selective preparation of normal-, tautomer-, and dual-fluorescent molecules with common ESIPT core. 2'-Hydroxyacetophenone (OHAP) is known as a typical molecule to undergo excited-state intramolecular hydrogen transfer (ESIPT) to emit fluorescence from excited state tautomer. In this study, a series of OHAP-cored fluorescent molecules 1-10 have been prepared and their excited state properties have been explored. The bathochromic shift of π–π* absorption band with π–extension of substituents indicates that the excitation energy of the normal form of OHAP unit is reduced due to the substituents, while the energy of excited tautomer is likely to be independent on π–extension of substituents. When pyrene or anthracene was connected at the end (4 and 5), only normal fluorescence was appeared in the exchange for disappearance of the tautomer fluorescence. An anthracene derivative 10 shows dual fluorescence, indicating that the normal and the tautomer excited states are energetically "balanced". The fluorescence lifetime analysis revealed the ESIPT reaction rate of 10 is much slower compared to other derivatives and the normal and tautomer form was in equilibrium in the excited state.

Introduction

The aim of this paper is to provide basic insights about selective preparation of normal-, tautomer-, and dual-fluorescent molecules having excited state intramolecular proton transfer (ESIPT) core. ESIPT is one of the most fundamental and important photochemical process providing proton-transfered tautomer in the excited state.[1] Typically, ESIPT molecules contain vicinally-substituted hydrogen donors and acceptors that forms intramolecular hydrogen bond in its ground state. The ESIPT is induced by intramolecular electronic re-distribution due to photoexcitation.[2] The significant features of ESIPT is to proceed ultrafast ($k > 10^{12}$ s^{-1}) to yield excited tautomer that emits fluorescence that is not re-absorbed due to non-overlap of the absorption and fluorescence bands.[3] An immediate back proton transfer reaction of ground state tautomer to an original normal form takes place[4] to complete four-level photochemical scheme (Figure 1a). The mechanism of the ESIPT is still being explored for understanding the photophysical and photochemical properties of ESIPT compounds.

ESIPT molecules have shown great versatility in a wide range of applications including laser dye,[5] photostabilizer,[6] UV filter,[7] and probes for metal ion,[8] bioimaging,[9] and solvation dynamics.[10] Recent attempts have been made to achieve white light generation by dual fluorescent ESIPT molecules,[11] and that seems to be the recent front line of this research area.

One unique phenomenon associated with ESIPT molecules is the dual fluorescence, which is ascribed to emission from the excited state of both normal and tautomer forms, and thus needs the energetically "balanced" normal- and tautomer-excited states (Figure 1b), and making such a balance is one challenging issue in this field. From the molecular design point of view, it would be possible to reduce the normal form excited state energy to achieve energetically balanced excited state that emit dual fluorescence. In this study, we focused on targeting construction of dual-fluorescent ESIPT chromophore. The results would provide an insight into selective preparation for normal- (Figure 1c), tautomer-, or dual fluorescent molecule.

Our simple idea is to introduce a series of π-extended arylethynyl substituents to 2-hydroxyacetophenone (OHAP), one of typical and photochemically stable ESIPT unit (Figure 2) that is known to exhibit strong hydrogen bonding between

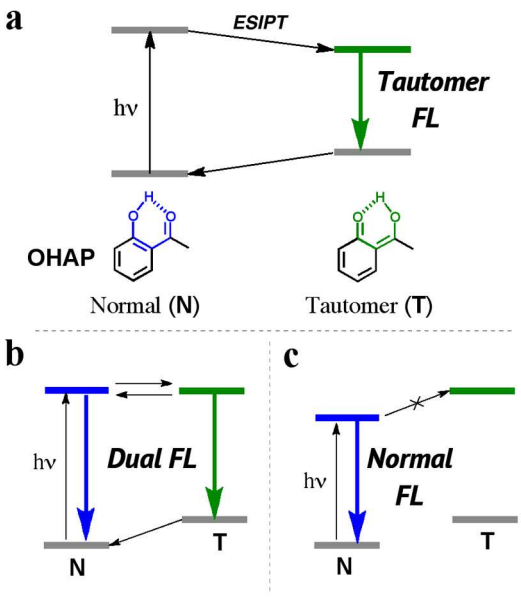

Figure 1. Potential energy diagram for 2-hydroxyacetophenone (a), dual fluorescent ESIPT molecules (b), and normal fluorescent molecules in which ESIPT reaction is energitically unfavorable (c).

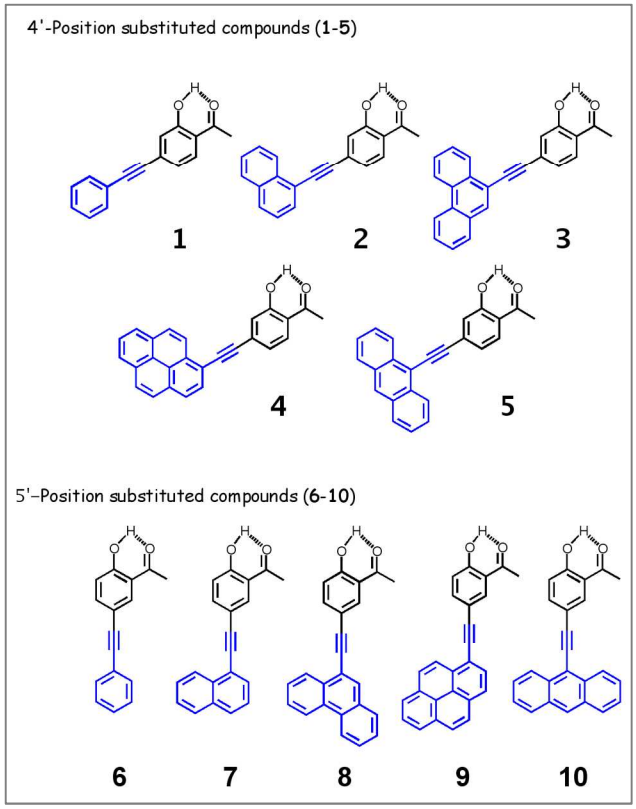

Figure 2. Chemical structures of compounds **1-10**.

neighboring hydroxyl and carbonyl groups.[12] As more π-extended substituents introduced, the π–π* transition energy of the normal form of OHAP unit will be reduced and consequent bathochromic shift of π–π* absorption band is assumed.

Results and Discussion

A series of arylethynyl-substituted 2-hydroxyacetophenones were prepared from Sonogashira cross coupling of 4-bromo-2-hydroxyacetophenone (for **1-5**) or 5-bromo-2-hydroxyacetophenone (for **6-10**) with corresponding aryl acetylene (Scheme S1). The photophysical data of **1-10** are listed in Table 1.

Effect of substituent on photochemical and photophysical properties

First, we compared the absorption and fluorescence bands of **1** and **2**. (Figure 3a and 3b) As expected, bathochromic shift of the absorption band was observed in **2**. In contrast, the fluorescence bands attributed to the excited tautomer of **1** and **2** were almost identical, indicating that the energy of excited tautomer is likely to be independent on π–extension of substituents. The similar results were obtained with phenanthrene derivative **3** (Figure 3c). When pyrene or anthracene was connected at the end (**4** and **5**), only normal fluorescence was appeared in the exchange for disappearance of the tautomer fluorescence (Figure 3d and 3e). This phenomenon can be explained by considering the π-extension at the end mainly reduce the excited state energy of normal form but not to tautomer form: due to the π–extension, ESIPT reaction in **4** and **5** become energetically unfavorable. An energy diagram for compounds **1-5** was summarized in Figure 3f. This notion prompted us to prepare another (5'-substitution) series of molecules **6-10**. The absorption and fluorescence spectra for **6-10** (Figure 3g-k) shows slightly different substituent effect than that observed in 4'-position substituted compounds **1-5**: the absorption band was red-shifted with π-extension of substituents, whereas tautomer fluorescence was observed even in pyrene was introduced (Figure 3j). The result indicates that the excited state energy of normal form in **9** is still higher compared to that of tautomer. This is probably because the tautomer energy of 5'-substitution compounds **6-10** is less than those of 4'-substitution series **1-5**, as can be expected from the fluorescence spectra, of which the maximum of the tautomer emission band of **6-10** are at longer wavelength compared to those of **1-3**. Finally, in anthracene derivative **10,** the dual fluorescence around 475 and 550 nm was observed (Figure 3k). According to these results, this dual fluorescence indicates the excited state energy of normal and tautomer form become close by introduction of anthrylethynyl group. To further evaluate the dynamics, the fluorescence decay (λ_{ex} = 375 nm) of **10** was monitored. At "normal" fluorescence region (450 nm) of **10**, decay curve was analyzed as two components with lifetimes of 27 and 547 ps. The 27 ps decay component was disappeared when monitored at the "tautomer" region (650 nm), where -25 ps of rise and slow decay (549 ps) component were observed. According to the normal (Figure 3e) and tautomer (Figure 3g-j) fluorescence spectra, the fluorescence decay of **10** can be selectively monitored at each wavelength (450 and 650 nm) without overlap for normal and tautomer fluorescence. Despite that, the lifetime of the slow decay component at normal and tautomer regions of **10** were almost identical. These results strongly support that equilibrium

Table 1. Spectroscopic, photophysical and photochemical data for **OHAP** and compounds **1-10** (benzene solution, 298 K)

Compds	λ_{abs}/nm (ε/10^4 $M^{-1}cm^{-1}$)	λ_{fl}/nm (Φ_f/10^{-3})	ΔE_{SS}/cm^{-1}	τ_s/ps	k_{fl}/$10^7 s^{-1}$	k_+/$10^{10} s^{-1}$	k_-/$10^9 s^{-1}$
OHAP	327 (0.42)	520 (0.94)	11400	67	1.4	-[g]	-
1	314 (2.6), 348 (1.3)	520 (11)	9500	605	1.8	-[g]	-
2	345 (3.0), 365 (2.7)	520 (11)	8200	548	2.0	-[g]	-
3	347 (3.1), 368 (2.8)	520 (12)	7900	557	2.2	-[g]	-
4	385 (3.9), 410 (3.6)	440, 460 (550)	1660	1500	37	-[g]	-
5	413 (2.4), 437 (2.2)	458, 482 (530)	1050	2880	18	-[g]	-
6	307 (2.2), 354 (0.34)	548 (3.5)	10000	236	1.5	-[g]	-
7	323 (2.4), 343 (2.0)	550 (5.6)	9900	308	1.8	-[g]	-
8	325 (3.2), 345 (2.6)	552 (5.3)	9800	335	1.6	-[g]	-
9	367 (4.6), 390 (3.8)	554 (9.3)	7600	502	1.9	-[g]	-
10[a]	403 (2.0), 423 (1.7)	N: 463 (3.1) T: 556 (8.0)	810 5700	N[b]: 27 (0.82)[c] , 547 (0.18)[c] T[d]: -25,[e] 549	1.5[f] 1.5[f]	3.0 -	6.7 -

a: N and T indicates normal and tautomer form, respectively. *b*: monitored at 450 nm. *c*: preexponential factor *d*: monitored at 600 nm. *e*: minus sign indicates the rise component. *f*: rate constant for population decay (slower component). *g*: Rate constant values for ESIPT were not listed because it is too fast for our experimental set-up.

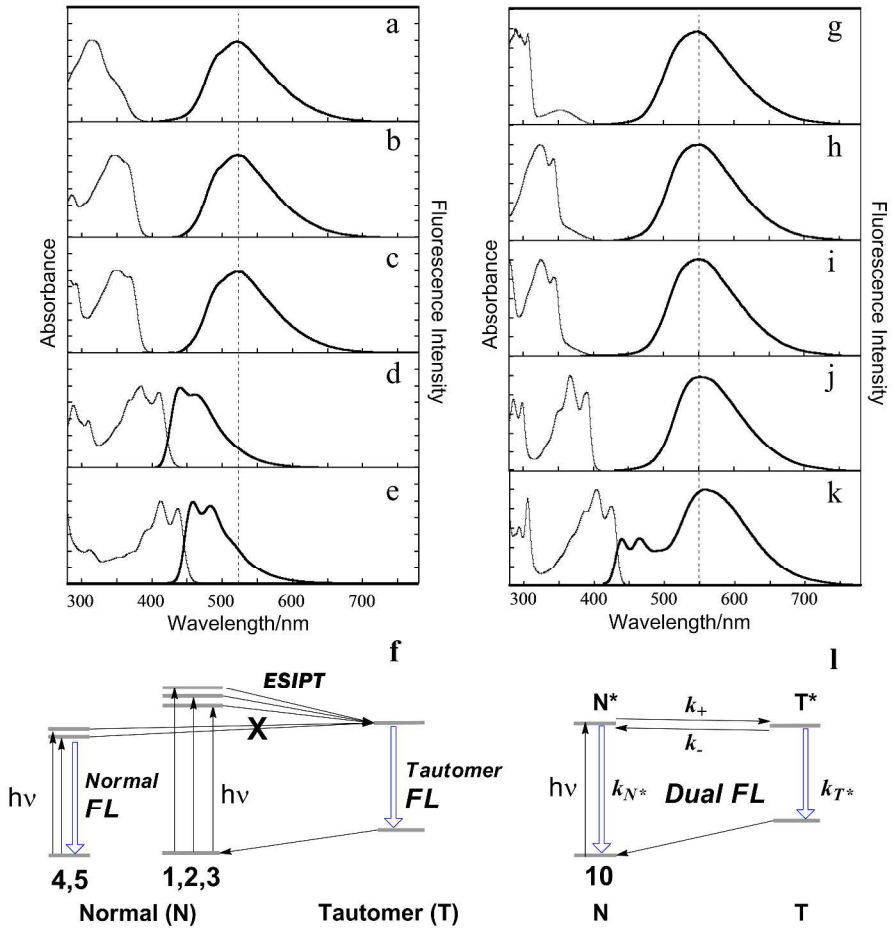

Figure 3. Absorption (thin line) and fluorescence (solid line) spectra of **1-5** in benzene under argon at room temperature (a-e). Potential energy diagram of excited state of **1-5** (f). Absorption and fluorescence spectra of **6-10** in the same conditions (g-k). Potential energy diagram of excited state of **10** (l, N*: normal species of excited state; T*: tautomer species of excited state; k_+: proton transfer rate constant; k_-: reverse proton-transfer rate constant; k_{N*}: decay rate constant of N* for all decay channel except k_+; k_{T*}: decay rate constant of T* for all decay channel except k_-).

of the excited-state normal and tautomer form is established, due to energetically close two excited states. The fast decay (27 ps at 450 nm) and rise (-25 ps at 650 nm) component could be attributed to the ESIPT process in the excited state, and the slower components commonly observed at 450 and 650 nm is

the population decay process after normal-tautomer equilibrium is established. Figure 3l expresses the energy diagram of **10**. It should also be noted that an equilibrium exists between the two excited states in **10** is probably a reflection of the existence of a near barrierless proton transfer. If there were a barrier between two excited states, the lifetime of normal and tautomer excited state should be different, even if two states were energetically equal.

Fluorescence spectra of **10** were measured in various solvents. As seen in benzene solution, dual fluorescence of **10** was also observed in hexane, THF, dichloromethane, acetonitrile (Figure S1). The intensity ratio of normal fluorescence and tautomer fluorescence depended on the solvent, due to different manner of interaction between excited state molecule and solvent molecule. Tautomer fluorescence band red-shifted in polar solvents, while normal fluorescence band did not shift considerably (Figure S1). This can be accounted for by assuming that the tautomer excited state is stabilized by polar solvents, probably because the tautomer excited state of **10** is more polar than the excited state of normal form.

Excited state dynamics of proton-transfer coupled reaction for compound 10.

In comparison with **1-9**, the relaxation dynamics of **10** are complicated due to establishment of the equilibrium between excited normal form and tautomer form. According to the reaction model shown in the Figure 3l, the differential rate equations for change of concentrations of normal and tautomer species can be expressed as follows: [11,13]

$$\frac{d[\mathrm{N}^*]}{dt} = -(k_{N^*} + k_+)\cdot[\mathrm{N}^*] + k_-\cdot[\mathrm{T}^*] \quad (1)$$

$$\frac{d[\mathrm{T}^*]}{dt} = -(k_{T^*} + k_-)\cdot[\mathrm{T}^*] + k_+\cdot[\mathrm{N}^*] \quad (2)$$

where k_+ and k_- denote the forward and reverse ESIPT rate, respectively, and k_{N^*} and k_{T^*} are decay rate for excited normal (N*) and tautomer (T*), respectively.

The integration of equations 1 and 2 with given initial conditions at $t = 0$, $[\mathrm{N}^*] = [\mathrm{N}^*]_0$ and $[\mathrm{T}^*] = [\mathrm{T}^*]_0 = 0$ gives the following equations for [N*] and [T*]:

$$[\mathrm{N}^*] = \frac{[\mathrm{N}^*]_0}{\lambda_2-\lambda_1}\{(\lambda_2 - X)exp(-\lambda_1 t) + (X-\lambda_1)exp(-\lambda_2 t)\} \quad (3)$$

$$[\mathrm{T}^*] = \frac{k_+[\mathrm{N}^*]_0}{\lambda_2-\lambda_1}\{exp(-\lambda_1 t) - exp(-\lambda_2 t)\} \quad (4)$$

Where,

$$\lambda_1 = \frac{(X+Y)-\sqrt{(X-Y)^2+4\cdot k_+\cdot k_-}}{2}$$

$$\lambda_2 = \frac{(X+Y)+\sqrt{(X-Y)^2+4\cdot k_+\cdot k_-}}{2}$$

$X = k_+ + k_{N^*}$, $Y = k_- + k_{T^*}$

With assumption of fast excited-state equilibrium between the normal and tautomer species (i.e., k_+ and $k_- \gg k_{N^*}$ and k_{T^*}, and thus $X \approx k_+$ and $Y \approx k_-$), λ_1 and λ_2 can be written as follows:

$$\lambda_1 \approx \frac{k_{N^*}+k_{T^*}\cdot K}{1+K} \quad (5)$$

$$\lambda_2 = k_+ + k_- \quad (6)$$

where K represents the equilibrium constant between N* and T*. Thus, upon excitation, initially generated N* should undergo two decay pathways with time constants of λ_1 (population decay) and λ_2 (fast dynamics). On the other hands, the dynamics of T* should be described with the rise and decay components with the time constants of λ_2 and λ_1, respectively. According to the substituent-independent tautomer fluorescence spectra (see Figure 3g-3k), the fluorescence lifetime monitored at 450 nm is obtained with no interference of the tautomer fluorescence. Therefore, the fast decay process with a rate constant of $3.7\text{x}10^{10}$ s^{-1} can be ascribed to λ_2 ($k_+ + k_-$), and the slower decay rate ($1.82\text{x}10^9$ s^{-1}) corresponds to the the population decay (λ_1) after excite state equilibrium between N* and T* is established. The preexponential factors for equation 3 can be further derived to

$$[\mathrm{N}^*]_0 \cdot \frac{X-\lambda_1}{\lambda_2-\lambda_1} \approx \frac{k_+}{k_+ + k_-} \quad (7)$$

$$[\mathrm{N}^*]_0 \cdot \frac{\lambda_2-X}{\lambda_2-\lambda_1} \approx \frac{k_-}{k_+ + k_-} \quad (8)$$

The ratio for equation 7 and 8 is equal to k_+ / k_- ($= K$). In addition, K is equivalent to the ratio of experimentally-obtained two preexponential factors that are 0.82 (for 27 ps, Table 1) and 0.18 (for 549 ps). Thus K vaule of **10** is calculated to be 4.56. Since $k_+ + k_-$ was 3.7×10^{10} s^{-1}, k_+ and k_- are 3.0×10^{10} s^{-1} and 6.7×10^9 s^{-1}, respectively.

The rate constant for ESIPT of **10** is one-order smaller than those of **5-9**, despite the same ESIPT chromophore, which can be a result of energetically proximity of both excited normal and tautomer forms. This is the first example of targeting production of dual fluorescent ESIPT molecules by conventional chemical modification approach. As a result, it was found that ESIPT reaction rate would be controllable by tuning the excited energy of normal form against corresponding tautomer form.

Conclusion

We demonstrated to prepare normal-, tautomer-, and dual-fluorescent molecules, by tuning of relative excited state energy of normal form with leaving those of tautomer form. The absorption and fluorescence spectra revealed that the energy of normal form is selectively reduced with π-extension, while those of tautomer form are not. In 4-position substitution series, ESIPT reaction no longer took place when pyrene or anthracene was placed at the end. In 5-substituted series, ESIPT took place in all derivatives. Exceptionally, anthracene

derivative **10** shows dual fluorescence and the fluorescence lifetime analysis revealed the ESIPT reaction rate of **10** is much slower compared to other derivatives and the normal and tautomer form was in equilibrium in the excited state. This approach for targetting dual fluorescence molecules may be applicable to other chromophores, because in many ESIPT chromophores have the driving forces of ESIPT reaction in common.

Experimental

Apparatus.

Sample solutions were prepared in benzene (Kanto Chemical) and deoxygenated by bubbling highly purified argon (>99.999%) through a needle. Fluorescence and excitation spectra were measured with an Hitachi F-4500 fluorescence spectrophotometer using a 1 cm × 1 cm quartz cuvette. Sample concentrations were adjusted to an absorbance of 0.05-0.1 at the absorption maximum. Absorption spectra were recorded with a Shimadzu UV-1600 spectrophotometer. Fluorescence decay measurements were performed using a time-correlated single-photon counting method. The apparatus was assembled based on the method previously described.[14,15] Excitation at 375 nm was achieved using a diode laser (PicoQuant, LDH-P-C-405) driven by a power control unit (PicoQuant, PDL 800-B) with a repetition rate of 2.5 MHz. Temporal profiles of fluorescence decay were recorded using a microchannel plate photomultiplier (Hamamatsu, R3809U) equipped with a TCSPC computer board module (Becker and Hickl, SPC630). The full-width at half-maximum (FWHM) of the instrument response function was 51 ps. Criteria for the best fit included $\chi 2$ values and Durbin–Watson parameters obtained by nonlinear regression.[16]

Materials.

All solvents used and 2-hydroxyacetophenone (OHAP), 4-bromo-2-hydroxyacetophenone, 5-bromo-2-hydroxyacetophenone, ethynylbenzene, 1-ethynylnaphtharene were purchased from Wako Pure Chemical Industries Ltd., Japan or Aldrich, USA and were used without further purification. 9-Ethynylphenanthrene,[17] 1-ethynylpyrene,[18] and 9-ethynylanthracene[19] were prepared as reported previously.

1-(2-Hydroxy-4-(2-phenylethynyl)phenyl)ethanone (1).

A mixture of 4-bromo-2-hydroxyacetophenone (2.73 g, 12.7 mmol), ethynylbenzene (1.93 g, 18.9 mmol), $Pd(PPh_3)_2Cl_2$ (461 mg, 0.657 mmol), PPh_3 (83.0 mg, 0.316 mmol), and triethylamine (2.54 g, 25.1 mmol) in dry THF (50 mL) was stirred for 30 min at room temperature under nitrogen. After addition of CuI (74.9 mg, 0.393 mmol), the mixture was further stirred for 24 h. The reaction was quenched by addition of water and was extracted with dichloromethane for three times. The organic layer was then washed with saturated $NaHCO_3$aq, dried over $MgSO_4$, filtered, and evaporated. The residue was purified with silica gel column chromatography (eluent: chloroform/hexane = 1:2) to give desired product (1.21 g, 40% yield) as pale orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.66 (s, 3H), 7.06 (dd, *J* = 8.3 Hz, *J* = 1.4 Hz, 1H), 7.15 (d, *J* = 1.4 Hz, 1H), 7.38-7.40 (m, 3H), 7.56-7.58 (m, 2H), 7.72 (d, *J* = 8.3 Hz, 1H), 12.31 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.7, 88.4, 93.1, 119.2, 121.1, 122.1, 122.5, 128.5 (2C), 129.0, 130.6, 131.3, 131.9 (2C), 162.1, 203.9. Anal. Calcd. for $C_{16}H_{12}O_2$ (236.27): C, 81.34; H, 5.12. Found: C, 81.15; H, 5.15.

1-(2-Hydroxy-4-(2-(naphthalen-1-yl)ethynyl)phenyl)ethanone (2).

A mixture of 4-bromo-2-hydroxyacetophenone (542 mg, 2.52 mmol), ethynylbnaphtharene (595 mg, 3.91 mmol), $Pd(PPh_3)_2Cl_2$ (91.5 mg, 0.130 mmol), PPh_3 (18.5 mg, 0.0705 mmol), triethylamine (512 mg, 5.05 mmol) in dry THF (10 mL) was stirred for 20 min at room temperature under nitrogen. After addition of CuI (16.3 mg, 0.086 mmol), the mixture was further stirred for 24 h. The reaction was quenched by addition of water and was extracted with dichloromethane for three times. The organic layer was then washed with saturated $NaHCO_3$aq, dried over $MgSO_4$, filtered, and evaporated. The residue was purified with silica gel column chromatography (eluent: dichloromethane/hexane = 1:2) to give desired product (172 mg, 21% yield) as pale orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.67 (s, 3H), 7.17 (dd, *J* = 8.1 Hz, *J* = 1.4 Hz, 1H), 7.27 (d, *J* = 1.4 Hz, 1H), 7.50.(t, *J* = 8.3 Hz, 1H), 7.58 (t, *J* = 8.1 Hz, 1H), 7.64 (dd, *J* = 8.3 Hz, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.81 (dd, *J* = 8.1 Hz, *J* = 1.4 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 8.42 (d, *J* = 8.1 Hz, 1H), 12.35 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.7, 91.4, 93.3, 119.3, 120.1, 121.1, 122.1, 125.3, 126.0, 126.6, 127.1, 128.4, 129.6, 130.7, 131.0, 131.4, 133.20, 133.24, 162.2, 203.9. Anal. Calcd. for $C_{20}H_{14}O_2$ (286.32): C, 83.90; H, 4.93. Found: C, 83.65; H, 5.03.

1-(2-Hydroxy-4-(2-(phenanthren-10-yl)ethynyl)phenyl)ethanone (3)

A mixture of 4-bromo-2-hydroxyacetophenone (541 mg, 2.52 mmol), 9-ethynylphenanthrene (1.02 g, 5.04 mmol), $Pd(PPh_3)_2Cl_2$ (92.5 mg, 0.132 mmol), PPh_3 (25.1 mg, 0.098 mmol), CuI (16.3 mg, 0.086 mmol), triethylamine (13 mL) was dissolved in dry THF (13 mL). The solution were degassed by three freeze-pump-thaw cycles to remove oxygen. After warming up to room temperature, the solution was stirred for 24 h under nitrogen. The reaction was quenched by addition of water and was extracted with dichloromethane for three times. The organic layer was then washed with saturated $NaHCO_3$aq, dried over $MgSO_4$, filtered, and evaporated. The residue was purified with silica gel column chromatography (eluent: dichloromethane/hexane = 1:2) to give desired product (660 mg, 78% yield) as pale orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.67 (s, 3H), 7.19 (dd, *J* = 8.1 Hz, *J* = 1.5 Hz, 1H), 7.30 (d, *J* = 1.5 Hz, 1H), 7.64 (t, *J* = 8.1 Hz, 1H), 7.69-7.76 (m, 4H), 7.90 (dd, *J* = 7.8 Hz, *J* = 1.3 Hz, 1H), 8.13 (s, 1H), 8.49-8.53 (m, 1H), 8.68-8.75 (m, 2H),

12.36 (s, 1H). ^{13} C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.7, 91.6, 92.9, 118.9, 119.3, 121.2, 122.1, 122.7, 122.9, 126.8, 127.1, 127.26, 127.28, 127.9, 128.8, 130.1, 130.6, 130.7, 130.9, 131.1, 131.3, 132.7, 162.2, 203.9.
Anal. Calcd. for $C_{24}H_{16}O_2$ (336.38): C, 85.69; H, 4.79. Found: C, 85.42; H, 4.80.

1-(2-Hydroxy-4-(2-(pyren-1-yl)ethynyl)phenyl)ethanone (4)
A mixture of 4-bromo-2-hydroxyacetophenone (751 mg, 3.49 mmol), 1-ethynylpyrene (1.21 g, 5.36 mmol), $Pd(PPh_3)_2Cl_2$ (177 mg, 0.253 mmol), PPh_3 (113 mg, 0.430 mmol), CuI (104 mg, 0.548 mmol), triethylamine (40 mL) was dissolved in dry THF (30 mL). The solution were degassed by three freeze-pump-thaw cycles to remove oxygen. After warming up to room temperature, the solution was stirred for 48 h under nitrogen. The reaction was quenched by addition of water and was extracted with dichloromethane for three times. The organic layer was then washed with saturated $NaHCO_3$aq, dried over $MgSO_4$, filtered, and evaporated. The residue was purified with silica gel column chromatography (eluent: chloroform/toluene = 1:1) to give desired product (684 mg, 54% yield) as pale orange solid.
^{1} H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.66 (s, 3H), 7.20 (dd, *J* = 8.1 Hz, *J* = 1.5 Hz, 1H), 7.32 (d, *J* = 1.5 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 8.04-8.07 (m, 2H), 8.11-8.15 (m, 2H), 8.20-8.26 (m, 4H), 8.62 (d, *J* = 9.1 Hz, 1H), 12.37 (s, 1H). ^{13} C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.7, 92.6, 94.1, 116.8, 119.2, 121.1, 122.1, 124.2, 124.4, 124.6, 125.3, 125.85, 125.92, 126.4, 127.2, 128.6, 128.7, 129.9, 130.7, 131.0, 131.2, 131.5, 131.8, 132.2, 162.2, 203.9.
Anal. Calcd. for $C_{26}H_{16}O_2$ (360.40): C, 86.65; H, 4.47. Found: C, 86.86; H, 4.51.

1-(4-(2-(Anthracen-10-yl)ethynyl)-2-hydroxyphenyl)ethanone (5)
A mixture of 4-bromo-2-hydroxyacetophenone (458 mg, 2.13 mmol), 9-ethynylanthracene (847 mg, 4.19 mmol), $Pd(PPh_3)_2Cl_2$ (80.0 mg, 0.115 mmol), PPh_3 (26 mg, 0.099mmol), CuI (27 mg, 0.14 mmol), triethylamine (10 mL) was dissolved in dry THF (11 mL). The solution were degassed by three freeze-pump-thaw cycles to remove oxygen. After warming up to room temperature, the solution was stirred for 48 h under nitrogen. The reaction was quenched by addition of water and was extracted with dichloromethane for three times. The organic layer was then washed with saturated $NaHCO_3$aq, dried over $MgSO_4$, filtered, and evaporated. The residue was purified with silica gel column chromatography (eluent: chloroform/hexane = 1:2) to give desired product (198 mg, 28% yield) as pale orange solid.
^{1} H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.69 (s, 3H), 7.28 (dd, *J* = 8.1 Hz, *J* = 1.5 Hz, 1H), 7.39 (d, *J* = 1.5 Hz, 1H), 7.55 (td, *J* = 8.5 Hz, *J* = 1.0 Hz, 2H), 7.64 (td, *J* = 8.6 Hz, *J* = 1.1 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 2H), 8.49 (s, 1H), 8.62 (dd, *J* = 8.6 Hz, *J* = 1.1 Hz, 2H), 12.38 (s, 1H). ^{13} C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.7, 90.2, 99.7, 116.2, 119.3, 121.0, 122.0, 125.8, 126.5, 127.0, 128.77, 128.83, 130.8, 131.2, 131.5, 132.9, 162.2, 203.9.
Anal. Calcd. for $C_{24}H_{16}O_2$ (336.38): C, 85.69; H, 4.79. Found: C, 85.44; H, 4.79.

1-(2-Hydroxy-5-(2-phenylethynyl)phenyl)ethanone (6)
A mixture of 5-bromo-2-hydroxyacetophenone (2.26 g, 10.5 mmol), ethynylbenzene (2.58 g, 25.3 mmol), $Pd(PPh_3)_2Cl_2$ (528 mg, 0.752 mmol), PPh_3 (338 mg, 1.29 mmol), CuI (315 mg, 0.532 mmol), triethylamine (70 mL) was dissolved in dry THF (45 mL). The solution were degassed by three freeze-pump-thaw cycles to remove oxygen. After warming up to 60 °C, the solution was stirred for 6 h under nitrogen. The reaction was quenched by addition of water and was extracted with dichloromethane for three times. The organic layer was then washed with saturated $NaHCO_3$aq, dried over $MgSO_4$, filtered, and evaporated. The residue was purified with silica gel column chromatography (eluent: chloroform/hexane = 1:2) to give desired product (1.84 g, 74% yield) as pale orange solid.
^{1} H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.67 (s, 3H), 6.99 (d, *J* = 8.6 Hz, 1H), 7.36-7.35 (m, 3H), 7.354-7.456 (m, 2H), 7.64 (dd, *J* = 8.6 Hz, *J* = 2.0 Hz, 1H), 7.94 (d, *J* = 2.0 Hz, 1H), 12.41 (s, 1H). ^{13} C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.7, 88.2, 88.4, 114.1, 118.9, 119.6, 123.1, 128.36, 128.44, 131.5, 134.1, 139.3, 162.3, 204.2 .
Anal. Calcd. for $C_{16}H_{12}O_2$ (236.27): C, 81.34; H, 5.12. Found: C, 81.45; H, 5.13.

1-(2-Hydroxy-5-(2-(naphthalen-1-yl)ethynyl)phenyl)ethanone (7)
A mixture of 5-bromo-2-hydroxyacetophenone (1.51 g, 10.5 mmol), 1-ethynylnaphthalene (2.19 g, 14.4 mmol), $Pd(PPh_3)_2Cl_2$ (353 mg, 0.502 mmol), PPh_3 (227 mg, 0.864 mmol), CuI (199 mg, 01.04 mmol), triethylamine (70 mL) was dissolved in dry THF (45 mL). The solution were degassed by three freeze-pump-thaw cycles to remove oxygen. After warming up to 60 °C, the solution was stirred for 4 h under nitrogen. The reaction was quenched by addition of water and was extracted with dichloromethane for three times. The organic layer was then washed with saturated $NaHCO_3$aq, dried over $MgSO_4$, filtered, and evaporated. The residue was purified with silica gel column chromatography (eluent: chloroform/hexane = 1:2) to give desired product (1.49 g, 74% yield) as pale orange solid.
^{1} H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.71 (s, 3H), 7.04 (d, *J* = 8.8 Hz, 1H), 7.49 (dd, *J* = 7.8 Hz, *J* = 7.7 Hz, 1H), 7.57 (dd, *J* = 8.6 Hz, *J* = 8.1 Hz, 1H), 7.63 (dd, *J* = 8.8 Hz, *J* = 8.1 Hz, 1H), 7.76 (dd, *J* = 7.8 Hz, *J* = 7.7 Hz, 2H), 7.88 (t, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 2.0 Hz, 1H), 8.44 (d, *J* = 8.6 Hz, 1H), 12.45 (s, 1H). ^{13} C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.8, 86.6, 93.0, 114.2, 119.0, 119.7, 120.7, 125.3, 126.1, 126.5, 126.8, 128.4, 128.9, 130.4, 133.2, 133.3, 134.1, 139.4, 162.5, 204.2.
Anal. Calcd. for $C_{20}H_{14}O_2$ (286.32): C, 83.90; H, 4.93. Found: C, 83.90; H, 4.99.

1-(2-Hydroxy-5-(2-(phenanthren-9-yl)ethynyl)phenyl)ethanone (8)

A mixture of 5-bromo-2-hydroxyacetophenone (1.17g, 5.43 mmol), 9-ethynylphenanthrene (1.55 g, 7.66 mmol), $Pd(PPh_3)_2Cl_2$ (190 mg, 0.271 mmol), PPh_3 (76 mg, 0.29 mmol), CuI (64 mg, 0.10 mmol), triethylamine (40 mL) was dissolved in dry THF (26 mL). The solution were degassed by three freeze-pump-thaw cycles to remove oxygen. After warming up to 40 °C, the solution was stirred for 24 h under nitrogen. The reaction was quenched by addition of water and was extracted with dichloromethane for three times. The organic layer was then washed with saturated $NaHCO_3$aq, dried over $MgSO_4$, filtered, and evaporated. The residue was purified with silica gel column chromatography (eluent: chloroform/hexane = 1:1) to give desired product (1.04 g, 57% yield) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.71 (s, 3H), 7.05 (d, *J* = 8.8 Hz, 1H), 7.63 (dd, *J* = 7.0 Hz, *J* = 6.8 Hz, 1H), 7.67-7.79 (m, 4H), 7.89 (d, *J* = 6.8 Hz, 1H), 8.05 (d, *J* = 2.0 Hz, 1H), 8.10 (s, 1H), 8.52-8.56 (m, 1H), 8.678.75 (m, 2H), 12.46 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.8, 86.8, 92.7, 114.2, 119.0, 119.5, 119.7, 122.7, 122.9, 126.9, 127.06, 127.10, 127.2, 127.6, 128.6, 130.2, 130.3, 131.0, 131.3, 131.9, 134.1, 139.4, 162.5, 204.2.

Anal. Calcd. for $C_{24}H_{16}O_2$ (336.38): C, 85.69; H, 4.79. Found: C, 85.56; H, 4.98.

1-(2-Hydroxy-5-(2-(pyren-1-yl)ethynyl)phenyl)ethanone (9)

A mixture of 5-bromo-2-hydroxyacetophenone (1.17g, 5.43 mmol), 1-ethynylpyrene (729 mg, 3.39 mmol), $Pd(PPh_3)_2Cl_2$ (172 mg, 0.245 mmol), PPh_3 (114 mg, 0.434 mmol), CuI (100 mg, 0.525 mmol), triethylamine (40 mL) was dissolved in dry THF (35 mL). The solution were degassed by three freeze-pump-thaw cycles to remove oxygen. After warming up to 60 °C, the solution was stirred for 24 h under nitrogen. The reaction was quenched by addition of water and was extracted with dichloromethane for three times. The organic layer was then washed with saturated $NaHCO_3$aq, dried over $MgSO_4$, filtered, and evaporated. The residue was purified with silica gel column chromatography (eluent: chloroform/hexane = 1:1) to give desired product (1.28 g, 50% yield) as orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.68 (s, 3H), 7.03 (d, *J* = 8.6 Hz, 1H), 7.77 (dd, *J* = 8.6 Hz, *J* = 2.0 Hz, 1H), 8.02-8.05 (m, 3H), 8.09-8.14 (m, 2H), 8.18-8.24 (m, 4H), 8.64 (d, *J* = 9.1 Hz, 1H), 12.46 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.7, 87.7, 93.9, 114.3, 117.6, 119.0, 119.6, 124.3, 124.5, 124.6, 125.4, 125.7, 126.3 (2C), 127.3 (2C), 128.2, 128.4, 129.5, 131.1, 131.3, 131.8, 134.0, 139.4, 162.4, 204.2.

Anal. Calcd. for $C_{26}H_{16}O_2$ (360.40): C, 86.65; H, 4.47. Found: C, 86.60; H, 4.69.

1-(5-(2-(Anthracen-10-yl)ethynyl)-2-hydroxyphenyl)ethanone (10)

A mixture of 5-bromo-2-hydroxyacetophenone (848 mg, 3.95 mmol), 9-ethynylanthracene (1.17 mg, 5.38 mmol), $Pd(PPh_3)_2Cl_2$ (146 mg, 0.208 mmol), PPh_3 (51.4 mg, 0.196 mmol), CuI (100 mg, 0.525 mmol), triethylamine (30 mL) was dissolved in dry THF (20 mL). The solution were degassed by three freeze-pump-thaw cycles to remove oxygen. After warming up to 40 °C, the solution was stirred for 24 h under nitrogen. The reaction was quenched by addition of water and was extracted with dichloromethane for three times. The organic layer was then washed with saturated $NaHCO_3$aq, dried over $MgSO_4$, filtered, and evaporated. The residue was purified with silica gel column chromatography (eluent: chloroform/hexane = 1:1) to give desired product (80 mg, 66% yield) as orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.73 (s, 3H), 7.07 (d, *J* = 8.6 Hz, 1H), 7.54 (dd, *J* = 8.2 Hz, *J* = 8.1 Hz, 2H), 7.63 (dd, *J* = 8.7 Hz, *J* = 8.1 Hz, 2H), 7.85 (dd, *J* = 8.6 Hz, *J* = 2.0 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 2H), 8.10 (d, *J* = 2.0 Hz, 1H), 8.45 (s, 1H), 8.64 (d, *J* = 8.7 Hz, 2H), 12.45 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.8, 85.4, 99.4, 114.4, 117.1, 119.1, 119.7, 125.7, 126.66, 126.68, 127.8, 128.8, 131.2, 132.6, 133.9, 139.4, 162.5, 204.2.

Anal. Calcd. for $C_{24}H_{16}O_2$ (336.38): C, 85.69; H, 4.79. Found: C, 85.34; H, 4.86.

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