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Full Length Article

Enhanced solid state emission of quinoline derivatives for fluorescent sensors

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ABSTRACT

Excited-state intramolecular proton transfer (ESIPT) molecules are of utmost interest in the fields of organic light emitting diode, photo-patterning, chemosensor, proton transfer laser, and photostabilizer. Fine control of the functional substituents as well as the molecular structure of core ESIPT unit is primarily demanded for specific applications. Here, the photophysics of quinoline derivatives of 2-quinolin-2-yl-phenol and 2-(8-chloroquinolin-2-yl)phenol is explored. Straightening the twist between the hydroxyphenyl and the quinoline moieties with the aid of the hydrogen bonding promoted the excited energy to flow through a radiative decay pathway via proton transfer to the nitrogen. Furthermore, close molecular packing of J-aggregates and thus resulted vibration restriction in a dense matter opens an ESIPT corridor and is characterized to show enhanced emission. The mechanism is applied to the selective Cu^{2+} or Fe^{2+} cation detection and further immunofluorescence labeling using avidin–biotin protein specific binding is demonstrated with the aid of nano self-assembly technique.

1. Introduction

Fluorescent materials have drawn numerous interests in diverse field due to their potential application. Most of all, a fluorescent organic nanoparticle have a higher potential in terms of material synthesis and further nanoparticle preparation. On the other hand, the fluorescence intensity decrease in organic nanoparticles commonly because fluorescence quenching processes such as exciton coupling, excimer formation, excitation energy migration to the impurity traps, and self-absorption. Among these quenching processes, self-absorption is pointed as a main culprit for the low fluorescence. So far, many enhanced fluorescent organic nanoparticles have been reported but the intermolecular interaction is still an important matter in a fluorescence quenching process [1–6].

Excited-state intramolecular proton transfer (ESIPT) is to be applied to resolve the fluorescence quenching problem in a condensed matter due to the characteristic four-level photophysical scheme incorporating the ground and excited states of two different tautomers. Fast proton transfer reaction from the excited enol (E^*) occurs to give the excited keto (K^*) tautomer in a subpicosecond time scale upon photoexcitation and it soon deliver photo energy and return to the ground state. ESIPT cycle normally results in the total exclusion of self-absorption and the large Stokes' shifted keto emission. These results, the ESIPT process can make organic nanoparticles without self-absorption [7,8].

The fluorescent materials used to investigate a biological mechanism of a cell are generally either organic molecules or inorganic semiconductors. Organic materials possess a serious drawback of the fluorescence quenching and inorganic materials have a cyto-toxicity problem. A new fluorescent material is developed to overcome these problems by introducing a heterocyclic structure of excited-state intramolecular proton transfer since the molecular structure showed remarkable photophysical property and anticipate it is applied in the fluorescence labeling.

Here, photophysical properties of quinoline derivatives and their enhanced photoluminescence are reported with their capability in the field of immunofluorescence labeling.

2. Experimental details

2.1. Materials

Benzene, borontribromide, 2-bromophenol, n-butyllithium, 2,8-dichloroquinoline, methyl iodide, sodium hydride, tetrakis (triphenylphosphine)palladium, triisopropyl borate, anhydrous tetrahydrofurane (THF), and anhydrous dichloromethane were purchased from Aldrich. All reagents purchased were used without further purification.

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2.2. Characterization

^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were obtained in $CDCl_3$ at 400 MHz and 100 MHz on a Bruker Avance 500. Multiplicity was denoted by s (singlet), d (doublet), and t (triplet). High resolution mass spectra were obtained with HP5890 series II. Elemental analysis was performed with Thermo Electron Flash EA 1112. UV/vis absorption spectra were recorded on a Varian Cary50 spectrometer. Luminescence spectra were collected on a Photon Technology International QM4 spectrometer with a xenon lamp as a light source. Thin solid films were spun-cast on hydrophilic glass surface at 1000 rpm and dried in vacuo. Single crystals were grown by slow evaporation of ethanol and the X-ray crystallographic data for the single crystals were collected (Jeonju Center, KBSI, Korea) on a SMART APEX CCD SYSTEM (Bruker) equipped with a graphite-monochromated Mo Kα (λ=0.71073 Å) radiation source and a nitrogen cold stream (200 K). The structure was solved by the direct method and refined by a full-matrix least-squares analysis using anisotropic thermal parameters for non-hydrogen atoms with the SHELXTL program (SHELXTL, ver. 5, Bruker AXS, Madison, Wisconsin). All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions.

2.3. Synthesis

2.3.1. 2-Methoxyphenylboronic acid (**1**)

2-Bromophenol was dissolved in dry tetrahydrofurane (THF). Sodium hydride was added in the solution at 0 °C and stirred for 30 min, and then methyl iodide was added later. The mixture was stirred for another 30 min at room temperature and it was poured onto ice-water and extracted three times with benzene. The benzene layer was washed with saturated aqueous ammonium chloride and brine and dried over magnesium sulfate.

Above synthesized 2-bromoanisole was dissolved in dry THF under Ar environment. To the mixture was added n-BuLi dropwise at −78 °C and the reaction mixture was stirred for 30 min. The lithio derivative was then cannulated into triisopropyl borate in diethyl ether and stirred for 30 min. The resulting mixture was warmed up to room temperature, treated with diluted hydrochloric acid (10%) solution followed by the extraction with ether. The organic layer was dried on sodium sulfate. Oily crude product was stored in refrigerator for 24 h and the unstable crystals were rapidly washed with cold pentane and dried in vacuo (yield: 80%). 400 MHz ^{1}H NMR (CDCl3): δ 3.85 (s, 3H), 6.70 (s, 2H), 6.85 (d, 1H), 7.00 (t, 1H), 7.40 (t, 1H), 7.85 (d, 1H).

2.3.2. 8-Chloro-2-(2-methoxyphenyl)quinoline (**2**)

2-Methoxyphenylboronic acid (**1**), 2,8-dichloroquinoline, and palladium catalyst (5 mol%) were placed in a two-necked round bottom flask charged with 7 ml of THF under argon and 4 ml of 1 M Na_2CO_3 solution was added into the flask. The reaction mixture was stirred for 48 h at 80 °C. After cooling, the reaction mixture was poured into methanol. The precipitate was isolated by filtration and washed with deionized water and methanol and dried under vacuo. 400 MHz ^{1}H NMR: δ 3.93 (s, 3H), 7.05 (d, 1H), 7.18 (t, 1H), 7.46 (m, 2H), 7.77 (d, 1H), 7.85 (d, 1H), 8.10 (m, 2H), 8.17 (d, 1H).

2.3.3. 2-(8-Chloroquinolin-2-yl)phenol (**CQ**)

A double-neck round-bottom flask with 8-chloro-2-(2-methoxyphenyl)quinoline (**2**) in anhydrous dichloromethane was charged with inert Ar gas. To the mixture was added borontribromide in dichloromethane dropwise at −78 °C. The reaction mixture was warmed up to room temperature and was stirred overnight. The reaction mixture was poured to ice-water and extracted with ether. The compound, 2-(8-chloroquinolin-2-yl) phenol, was purified by chromatography on a silica gel column with dichloromethane and ether and recrystallization to yield yellow needle shape crystals (yield 85%). ^{1}H NMR(400 MHz, $CDCl_3$): δ 6.99 (t, J=8.4, 6.8 Hz, 1H), 7.16 (d, J=7.2 Hz, 1H), 7.42 (t, J=6.8, 6.8 Hz, 1H), 7.49 (t, J=8, 7.6 Hz, 1H), 7.78 (d, J=8.4 Hz, 1H), 7.87 (d, J=7.6 Hz, 1H), 7.99 (d, J=8 Hz, 1H), 8.12 (d, J=9.2 Hz, 1H), 8.31 (d, J=8.8 Hz, 1H), 15.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.9, 118.4, 118.8, 119.0, 126.4, 126.5, 126.9, 127.7, 130.3, 131.8, 132.6, 137.9, 141.4, 158.3, 161.2; Anal. Calcd for: $C_{15}H_{10}NOCl$: C, 70.46; H, 3.94; N, 5.48 Found C, 70.49; H, 3.93; N, 5.47. HRMS (FAB): calculated M^+ 255.70; observed M^+ 256.05.

A hydrogen substituted compound, 2-quinolin-2-yl-phenol (**HQ**), was also synthesized according to the above synthetic procedure to get yellow needle shape crystals (yield 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.0 (t, J=7.2, 6.8 Hz, 1H), 7.13 (d, J=8.4 Hz, 1H), 7.4 (t, J=7.2, 6.8 Hz, 1H), 7.58 (t, J=6.8, 6.8 Hz, 1H), 7.77 (t, J=6.8, 7.2 Hz, 1H), 7.85 (d, J=8 Hz, 1H), 7.97 (d, J=7.6 Hz, 1H), 8.07

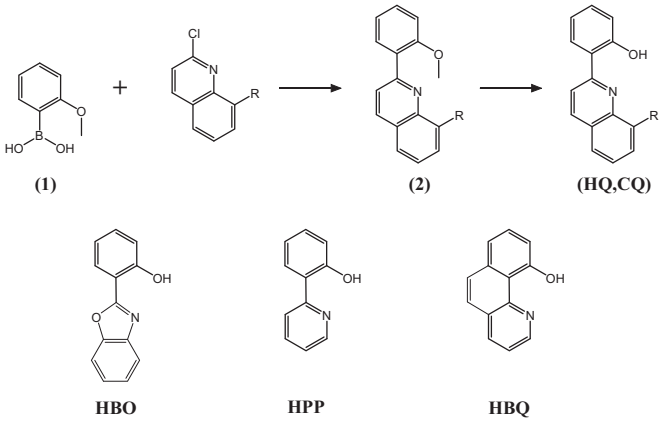

Fig. 1. Synthetic scheme of hydroxyphenyl quinoline, where R is H or Cl. And molecular structures of 2-(2-hydroxyphenyl)benzoxazole (HBO), 2-(2-hydroxyphenyl)pyridine (HPP), and 10-hydroxybenzoquinoline (HBQ) are shown.

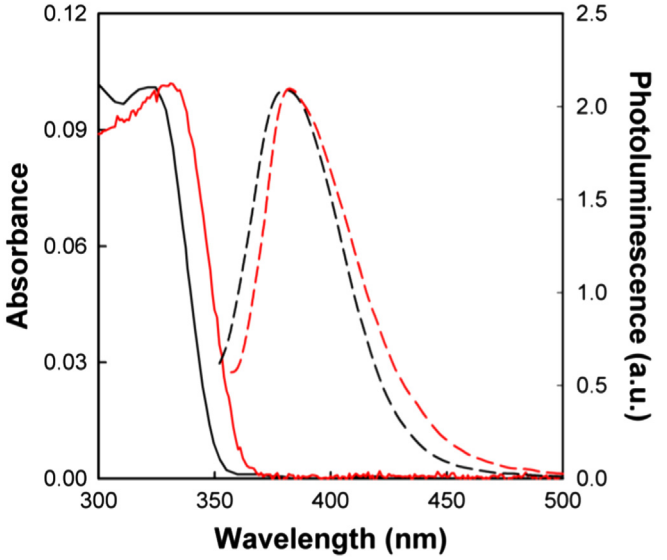

Fig. 2. UV/vis absorption (solid lines) and PL (dashed lines) spectra of methoxy-HQ (black) and methoxy-CQ (red) 10^{-5} M THF solution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).