AN ANALYSIS OF PHOTOPHYSICS OF AROMATIC FLUOROPHORES

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Abstract

According to Jablonski diagram (Jablonski 1935), emission of light from the lowest vibrational level of the first singlet excited state to the ground state is known as fluorescence and the fluorescent molecule follow the Kasha"s rule (Kasha 1950) and Franck-Condon principle (Lakowicz 1999). It was first observed by Sir John Frederick William Herschel in 1845 that the photoexcitation of a fluorophore leads to only single emission band (Kasha, 1950). However, later Lippert observed that 4-(N,N-dimethylamino)benzonitrile (DMABN) emits dual emission upon excitation at the near UV region (Lippert et al., 1961). The emission which appears at shorter wavelength is called „locally excited" (LE) emission and the longer wavelength emission is termed as „intramolecular charge transfer" (ICT) emission. Over the years, organic π-conjugated molecules find interest as building blocks for advanced optical materials and photovoltaic devices, as well as in molecular electronics (Tykwinski et al., 1998, Kivala et al., 2009, Beaujuge et al., 2010, Lin et al., 2012). Generally, π-conjugated organic fluorophores emit locally excited (LE) emission due to delocalization of the electron density over the whole molecule. Organic fluorophores, composed of donor and acceptor entities separated by a bridge, usually show LE emission as well as ICT transitions (Rettig 1986). In molecules with extended π-conjugation, the transition energies decrease as the extent of conjugation increases explained by Hückel molecular orbital theory (Hückel 1931).

Paper Identification

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Introduction

The acetylene bridged systems can be considered as an extended single bond system (Kottas et. al., 2005, Toyota 2010). Acetylene/ethynylene linkage has been extensively employed in recent years for developing various molecular scaffolds. The remarkable research interest in the acetylene chemistry is noticed because the triple bond connects two moieties linearly and with a minimum steric hindrance (Sipachev et. al., 2000). Moreover, the synthesis can be performed using convenient and efficient reaction methodologies like Sonogashira coupling, Corey-Fuchs reaction, alkyne metathesis, and elimination reaction (Bunz 2000). Acetylene- bridged aromatic systems have strong electronic interconnection between the peripheral aromatic moieties. Hence push-pull systems bridged

with acetylene linkage show efficient through bond charge transfer in the ground and excited states. The acetylene/alkynyl bridge is mainly used as a spacer; but it can also affect the resulting optoelectronic properties of the donor-acceptor or push-pull system (Tingare et. al., 2017, Cann et. al., 2017, Mai et. al., 2014).

Earlier studies reveal that diphenylacetylene (DPA) and its derivatives exhibit rich photophysical properties (Saltiel et al., 2012). DPA is one of those molecules which produce emission from higher electronic state (S2). The molecule shows a weak fluorescence due to the intersystem crossing between the S2 and almost non-emissive S1 excited state. However, unsymmetrically substituted DPA derivatives produce strong emission quantum yield (S0←S1) and strong photostability. Therefore, acetylene/ethynylene linker can help in designing novel chromophores that can be used in dye sensitized solar cells, organic light emitting diode, polymer light emitting diode, electro chemiluminiscent, multi-emitting fluorophore, chemical and biological sensor, fluorescent probe (Mai et. al., 2014, Tingare et. al., 2017, Yan et. al., 2016, Cann et. al., 2017).

Photophysics of Acetylene Containing Fluorophores

ICT dynamics in a push–pull diphenylacetylene (MTCN-DPA, Figure 1.1), which contains –SMe as donor and –CN as acceptor groups, was first investigated by Khundkar et al., (1990). The charge transfer occurs from the nonbonding orbital of S (nS) to the π antibonding orbital of CN (πCN^*). Later Broo (1994) carried out theoretical calculations on the ground and excited state geometries of MTCN-DPA. The ground state optimized geometry was found to be planar, while the excited state geometry was twisted in which the two phenyl rings were perpendicular to each other along the acetylene backbone.

Computed Excited State Geometries of DACN-DPA

Five excited singlet states of similar energies were computed for DACN-DPA by Lim and co-workers (Fujiwara et al., 2011). These states were $\pi\pi^*$, $\pi\sigma^*$, ICT, ICT(p), and ICT(σ^*), in the order of decreasing energy. In the ICT(σ^*) state, one electron is transferred from the donor dimethylaminobenzene part to the acceptor benzonitrile moiety. The dimethy laminobenzene is perpendicular to the benzonitrile part. The dipole moment of the ICT(σ^*) state is 24.7 D. Notably, the angle C(DMAB)CC is 135.0o, which deviates from the usual planarity. In the ICT state, the NMe2 group is perpendicular to the rest of the molecular entity. The ICT state has dipole moment 29.0 D. In the ICT(p) state the dimethylaminobenzene group is perpendicular to the benzonitrile, which is similar to the ICT(σ^*) state. However, it differs from the ICT(σ^*) state on the fact that the C(DMAB)C moiety is not bent. The oscillator strength (f = 1.18) of the ground state of the $\pi\pi^*$ is high and this state has dipole moment of 21.2 D. The $\pi\sigma^*$ is planar and it involves the transfer of electron from π to σ^* orbital, which is situated on the acetylene spacer. The $\pi\sigma^*$ has the lowest dipole moment (13.9 D) amongst the five excited singlet states.

Steady-State and Time-Resolved Fluorescence of DACN-DPA

The steady-state and time-resolved fluorescence spectra of DACN-DPA were studied. The absorption and fluorescence spectra are closely overlapped in hexane and mirror-image to each other. Thus, the emissive state was assigned to the S1 ($\pi\pi^*$) state. However, in CH3CN, the emission spectrum is significantly red-shifted. This indicated that the emission in CH3CN appears from a highly polar excited state. The temporal decay of the dye shows bi-exponential behavior with an ultrafast decay (1 ps) and a slower 849 ps component. The ultrafast decay observed by Lim and co-workers (Fujiwara et al., 2011) suggests the fast formation of the ICT excited

state. The ultrafast decay was not noted in n-hexane. The temporal profile shows a decay component of ~577 ps in n-hexane.

Photophysics of Diacetylene Containing Pull-push Fluorophores

Bylińska et al. studied the photophysics of pull-push fluorophores containing aromatic hydrocarbon and dimethylaniline linked by an acetylene unit in various solvents (Figure 1.2). The absorption spectra in various solvents showed structured band with maxima 22,780 cm–1 (360 nm) for naphthalene derivatives, while at 23,260 cm–1 (430 nm) for anthracene derivative. The absorption spectra showed bathochromic shift with an increase in the solvent polarity of around 750 and 550 cm–1 for naphthalene and anthracene derivatives, respectively. The emission spectra of all the fluorophores showed structured band in non-polar solvents, and bathochromic shift with increasing solvent polarity caused the disappearance of the vibronic structure. The emission spectra shift from about 27,400 cm–1 (365 nm) for iso-octane to 20,000 cm–1 (500 nm) in DMSO for both naphthalene derivatives, whereas from 22,200 cm–1 (450 nm) to 16,300 cm–1 (614 nm) for AacDMA. The derivatives showed high quantum yield as well as excited state dipole moment. The fluorescence lifetime values hover around 1–1.5 ns for naphthalene derivatives while 2–4 ns for AacDMA. The solute-solvent properties were studied using various polarity scales such as Reichardt's, Kamlet–Taft and Catalàn multi-parameter solvent scales. The change of hydrogen bond energy in the excited state was calculated using the solvatochromic method. Theoretical calculations confirmed the experimental results and showed that the fluorophores have planar conformation.

Photophysics of Donor-Acceptor Substituted Diphenylacetylene Fluorophores Szyszkowska et al. have synthesized the unsymmetrically substituted diphenylacetylene derivatives with different electron-acceptor substituent and studied their photophysics using various spectroscopic methods to understand the effect of the electron affinity of the substituents on the donor-acceptor pairs (Figure 1.3). The absorption and emission spectra of all the derivatives were recorded in solvents of varying polarities. The absorption maxima of these electron-acceptor derivatives shifted to longer wavelength in comparison to that of parent molecule DPA. The solvent polarity has little effect on the absorption band. The absorption maxima for PhacPhCOOMe were located at 294 nm and 297 nm in polar CH3CN and non-polar cyclohexane, respectively. The absorption spectrum was structured in non- polar cyclohexane and shows a red shift and less distinct vibronic structure in polar and protic solvents for electron-acceptor derivatives. The emission spectra of these derivatives exhibits well-formed vibronic structure in non-polar cyclohexane and bathochromic shift in polar solvents with loss of vibronic structure. The emission maximum band at 320 nm in cyclohexane red-shifted to around 360 nm in CH3CN for PhacPhCOOMe, and the band shifts from around 350 nm in cyclohexane to 450 nm in CH3CN for DMAPhacPh. Similarly, for DMAPhacPhCOOMe and DMAPhacPhCN the emission band maximum around 400 nm in cyclohexane shifts to 600 nm in acetonitrile.

EXPERIMENTAL METHODS

Synthesis and Photophysical Studies

The photophysical properties of the diacetylene bridged naphthalene–pyrene dyad NapBPy (see section 2.5.6 for synthetic details) were studied in nonaqueous solvents such as cyclohexane, acetonitrile (CH3CN), N,N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). The properties of NapBPy were compared with its constituent structures, two terminal acetylenes, Nap-yne and Py-yne as well as parent naphthalene and pyrene fluorophores (Figure 2.1). Nap-yne and Py-yne were synthesized using literature-reported protocols (Corey et. al., 1972). Parent pyrene

and naphthalene fluorophores were purchased from Sigma-Aldrich and SD Fine-Chem Limited, respectively, and used without further purification.The properties of NapBPy were also compared with a previously studied diacetylene bridged homodimer of pyrene (Benniston et. al., 2004) and a known diacetylene bridged homodimer of naphthalene (Cataldo et. al., 2010). The emission energy and quantum yield values of the diacetylene bridged pyrenyl dimer were taken from the literature (Benniston et. al., 2004). The emission energy and quantum yield of the diacetylene bridged naphthyl dimer were measured in our laboratory by synthesizing the known dye following the protocol similar to NapBPy. Spectroscopic grade solvents were used for all the photophysical studies. A stock solution of 10–3 M concentration was prepared in dichloromethane (DCM). The solutions in other solvents of different polarities were prepared by evaporating DCM from the desired amount of the stock solution by purging nitrogen gas. Then the desired solvent was added to it. The samples for the photophysical studies were prepared at room temperature in open atmosphere.

Steady-State Absorption and Fluorescence Experiments

Absorption spectra were recorded with a Shimadzu UV-2600 spectrometer. Fluorescence experiments were carried out with Horiba Jobin-Yvon FluoroMax-4 spectrofluorometer, with a 150 W xenon lamp as light source. The emission spectra were collected with slit widths of either 3/3 or 5/5 nm. An Aqualog Horiba Jobin-Yvon spectrophotometer was used for vapor sensing, having fixed scanning range and slit width with integration time 0.01 s and medium scan rate.

Time-Resolved Fluorescence Decay Experiments

Fluorescence lifetime was determined using Horiba Jobin-Yvon time-correlated, single- photon counting (TCSPC) lifetime instrument in reverse mode. For lifetime experiments, 295, 340, and 370 nm nano-LEDs were used as light sources. The instrumental full width at half-maximum of the nano-LEDs including the detector response was around 800 ps. The pulse repetition rate was set to 1 MHz. The instrument response function (IRF) was collected using a scatterer (Ludox AS40 colloidal silica). IBH software was used to analyze the decay data. A value of $\chi2$, $0.98 \leq \chi2 \leq 1.3$ was considered as a good fit, which was further judged by symmetrical distribution of residuals.

Computational Methodology

The computational studies were performed using Gaussian 09 computational package (Frisch et. al., 2010). Optimization of the ground state of the dyes was carried out using density functional theory (DFT) with B3LYP hybrid functional (Becke 1993) and 6-311G(d,p) basis set without any symmetry constrains. Vibrational analyses were carried out to ascertain the absence of imaginary frequencies. The effect of solvent was included through self-consistent reaction field (SCRF) using the polarizable continuum model (PCM).

General experimental section for synthesis:

Melting point was recorded using Sigma melting point apparatus in capillary tubes and was uncorrected. IR spectrum was recorded on JASCO FT-IR-4100 spectrometer. 1H (400 MHz) and 13C (100 MHz) NMR spectra of the dye NapBPy were recorded on Bruker Avance 400 spectrometer. The chemical shifts (δ ppm) and coupling constants (Hz) were calculated with reference to chloroform (CHCl3). In the 13C NMR spectra, the nature of the carbons (C, CH, CH2 or CH3) was ascertained by recording the DEPT-135 experiment and mentioned in the parentheses. High resolution mass measurement was performed using Micromass Q-ToF ESI instrument using direct inlet mode. Analytical thin-layer chromatography (TLC) was carried out on glass plates (7.5 x 2.5 and 7.5 x 5.0 cm) coated with Acme's silica gel G containing 13% calcium sulfate as binder or on pre-coated 0.2 mm

thick Merck 60 F245 silica plates. A combination of ethyl acetate and hexane was used as eluent. Visualization of spots was performed by exposure to iodine vapor. The dye was purified by silica gel [Acme's silica gel (100–200 mesh)] column chromatography.

Conclusion

In summary, the photophysical properties of a newly designed and synthesized diacetylene conjugated prototype electronic energy donor and acceptor pair were investigated. Naphthalene was used as a donor, and pyrene was used as an acceptor. The impact of the diacetylenic conjugation was evident by comparing the photophysical properties of the hybrid derivative with its constituent molecular structures, pyrenyl and naphthyl acetylenes, as well as parent pyrene and naphthalene chromophores. The salient outcomes of the present work are summarized below.

(1)   The hybrid derivative shows structured absorption and emission spectra in nonaqueous solvents, similar to its constituent molecular structures, terminal acetylenes. However, in contrast to parent pyrene chromophore or the pyrenyl acetylene, the hybrid derivative shows strongly allowed S0 → S1 transition. The improved photophysics of the dye was revealed in its much higher fluorescence quantum yield values, compared to parent pyrene and naphthalene as well as the terminal acetylenes.

(2)   In contrast to the earlier reported hetero diacetylenes in which ICT emission was observed in polar solvents, the naphthalene–pyrene dyad shows emission purely from an LE state in both nonpolar and polar organic media.

(3)   In addition to the LE emission in nonaqueous solvents, the dye shows an aggregate emission in mixed-aqueous solvents with higher percentage of water. This was evident from red-shifted absorption as well as emission band and a relatively longer fluorescence lifetime component compared to the LE state. Unlike the diacetylenic dye, the terminal acetylenes do not form aggregates in mixed-aqueous solvents.

(4)   In the aggregate form of the hybrid dye, the naphthyl moiety transfers its emission energy to the pyrenyl scaffold to some extent upon photoexcitation at 290 nm. This study demonstrates that it is possible to observe electronic energy transfer in a π-conjugated donor– acceptor dye by changing the chemical environment of the fluorophore.

(5)   Further, the excited-state photophysical properties of the hybrid dye were utilized for polar protic solvent vapor sensing in the solid state. The dye emits bluish white light in TLC plate as well as in Whatman paper, which changes to blue light when exposed to vapors of polar protic solvents such as MeOH, isopropanol, and EtOH.

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