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Multiple emissions from indenofluorenedione in solution and polymer films†

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A new indenofluorenedione derivative (IFO) with two weak electron-donating substituents was synthesized, and exhibited a multi-coloured emission including white. The multiple fluorescent channels can be controllably switched by changing the solvent and polymer matrix in a broad visible range. It was also demonstrated that IFO embedded in a polystyrene matrix is sensitive to environmental polarity, thus exhibiting the emission colour changes upon exposure to polar organic solvents.

Multicolour organic luminescent materials have attracted extensive attention due to their potential applications in flexible full-colour displays, next-generation lighting and bioimaging.¹ Compared with multicomponent molecular emitters, a single organic molecule eliciting multiple luminescences has many advantages such as no inherent phase separation, excellent colour stability, reproducibility and easy fabrication.² So far, several strategies have been proposed in this research area, that mainly rely on use of multiple channels or multiple signaling pathways such as an excimer or exciplex,³ excited-state intramolecular proton transfer⁴ and intra/inter-molecular charge transfer states.⁵ Among the above, a single molecule comprising electron-donor (D) and acceptor (A) units can be one of the simple and promising candidates for new colour tuneable fluorophores, because one can utilize emission from an intramolecular charge transfer (ICT) transition state.^{6,7} The ICT state, however, becomes a non-switchable deactivation pathway in many cases, resulting in showing red-shifted fluorescence due to positive solvatofluorochromism.^{7a} Therefore, an ICT molecule with blue emission arising from locally excited state (LE) is still limited, making it difficult to design a single organic

emitter with multiple emissions for the generation of white emission.

Indenofluorenedione is a rigid and planar π -conjugated molecule with electron-accepting ability, in which the $n-\pi^*$ and $\pi-\pi^*$ transition states lie very close to each other in non-polar solvents, and $\pi-\pi^*$ transition state is expected to be dominant in polar solvents.^{8,9} It occurred to us that by introducing the alkoxy phenyl moieties (weak electron-donor) at peripheral positions, the resultant D–A–D π -skeleton would afford alternative deactivation pathways *via* intra/inter-molecular ICT states, leading to multiple fluorescent channels.¹⁰ In this work, we report that an indenofluorenedione-based fluorophore (IFO) (Fig. 1a) having D–A–D framework exhibits unconventional blue emission from the LE state in dimethylformamide (DMF) and in

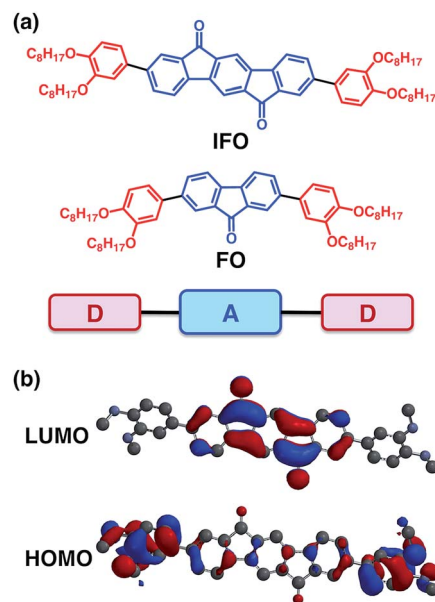


Fig. 1 (a) Chemical structures of IFO and FO with D–A–D arrangement; (b) HOMO and LUMO of IFO calculated at B3LYP/6-31G* level. The dodecyl groups are replaced by ethyl groups for simplicity.

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polysulfone matrix in addition to orange emission in methylcyclohexane (MCH), and red in *p*-xylene via intra/intermolecular ICT states. Compared to the fluorenone counterpart (FO), which is known to have forbidden radiative transition and exhibit special sensitivity towards solvent polarity,^{9,6c} IFO has an extended π -conjugated structure, enabling broader emission in visible range. The LE and ICT states of IFO can be switched by solvent polarity, which enables us to generate white emission. The LE-ICT state switching properties¹¹ of IFO can be also achieved in different polymer matrixes, resulting in multi-fluorescent polymer films.

The FO and IFO molecules were characterized by ¹H NMR, ¹³C NMR and elemental analysis (see Experimental section in ESI†). According to the DFT calculation (Fig. 1b), the HOMO of IFO is mostly delocalized on the electron-donating moiety and the LUMO is delocalized on the electron-accepting moiety. Photophysical properties of IFO in MCH, tetrahydrofuran (THF), DMF and *p*-xylene were summarized in Table 1 (also see Fig. S1, S2 and S5†).¹² The absorption spectrum of IFO consists of three peaks at 319, 369 and 530 nm (Fig. S1†); the peaks at 319 and 369 nm correspond to π - π^* transition of the indeno-fluorenedione core, which is consistent with the reported results.⁸ The absorbance of IFO at 369 nm is proportional to the concentration in the range from 5 μ M to 40 μ M in DCM, THF, DMF and *p*-xylene (Fig. S2†), indicating that there is no aggregates in the ground state under the experimental conditions. The absorption around at 530 nm can be assigned to ICT absorption; indeed when increasing the polarity of solvents from MCH to DMF, the absorption band exhibited solvatochromic shift (Fig. S1†). In stark contrast to the typical positive solvatochromic behaviours of conventional ICT molecules,^{7a} IFO showed unusual solvatochromic behaviour in polar solvent like DMF; a fluorescent band at 436 nm was observed, which is attributable to the transition from LE, S₁-S₀,¹³ while two low-energy emission peaks at 530 and 610 nm were observed in non-polar solvent like *p*-xylene (Fig. 2).

In order to assign the two emission peaks observed at longer wavelengths, the concentration dependence of fluorescence

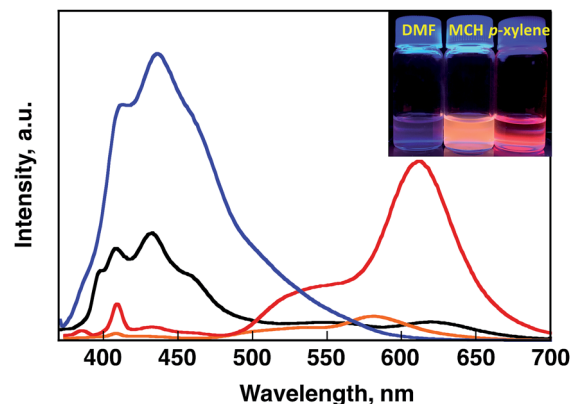


Fig. 2 Fluorescence spectra of IFO in various solvents (black: THF, orange: MCH, red: *p*-xylene, blue: DMF). [IFO] = 20 μ M excitation wavelength is 355 nm (inset: photographs under irradiation with 365 nm UV-lamp).

spectra of IFO was performed in *p*-xylene (Fig. S3a†). The solution of each concentration was excited at the wavelength, where the absorbance is around 0.2. We found that the fluorescent intensity at 610 nm is constant throughout the different concentrations (5 to 40 μ M). In contrast, the fluorescent intensity at 530 nm slightly increased along with increasing the IFO concentration (Fig. S3b†). These results indicate that fluorescent emissions at 530 and 610 nm in *p*-xylene are originating from the intermolecular events at the excited state and intramolecular charge transfer bands, respectively. The both charge transfer bands exhibited red shifts when medium changed from *p*-xylene to MCH. The three emissions from LE (436 nm) and charge transfer states (555 and 619 nm) were observed in THF (Fig. 2). The excitation spectra in various solvents were identical to the corresponding absorption spectrum (Fig. S4†).

We inferred that in MCH and *p*-xylene, the S₀-S₁ transition is n- π^* forbidden transition. Consequently, the excited deactivation pathway of IFO would be switched onto the intra- and intermolecular CT channels (Scheme S2†), leading to the low-energy

Table 1 Photophysical data of IFO and FO in various solvents

	Solvent	λ_{abs}^a (nm) ($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	λ_{em}^b (nm)	τ^c (ns)	Φ_{F}^d (%)
IFO	MCH	367 (2.9)	585	5.3	3.3
	<i>p</i> -Xylene	370 (2.9)	610	1.8	3.2
	THF	369 (2.7)	436	1.2	0.7
			619	0.5	
	DMF	369 (2.5)	436	3.4	2.2
FO	MCH	341 (3.2)	523	7.3	23
	<i>p</i> -Xylene	345 (3.2)	546	3.9	13
	THF	345 (3.2)	557	1.3	13
	DMF	347 (2.9)	422	2.4	3.3
			571	1.3	

^a Absorption maxima of π - π^* transition. ^b Emission maxima upon excitation at 355 nm for IFO and 345 nm for FO. ^c Fluorescent lifetimes calculated as average lifetimes. ^d Absolute fluorescence quantum yields determined by a calibrated integrating sphere system.

fluorescence with solvent-dependent characteristics (Table 1). The large dipole moment variation between the ground state and excited state of **IFO** is responsible for large Stokes shift observed in MCH (218 nm) and *p*-xylene (240 nm). Interestingly, in polar medium like DMF, the character of the lowest excited state of **IFO** changed to allow π - π^* transition (Scheme S2[†]). In this case, the CT band was not as favourably active as in non-polar solvents probably because of weak electron donating ability of dialkoxyphenyl groups.¹⁴ Instead, the LE with π - π^* character would play a major role in excited state deactivation mechanism. Thus, multiple fluorescent deactivation pathways of **IFO** can be switched by varying polarity of solvents. Commensurate with structural similarity, a fluorenone derivative (**FO**) exhibited similar solvatochromic behaviour (Fig. S6–S8[†]), but the extended π -conjugation length of **IFO** enables us to tune emission colour in wider range, particularly complementary blue (in DMF) and red (in *p*-xylene).

Such unusual solvatochromic behaviour inspires us to generate white emission in binary solvent mixtures. The desirable amount of **IFO** was added into binary solvents of DMF and *p*-xylene under various ratios. The total concentration of **IFO** was kept identical to be 20 μ M. All the solvent combinations showed similar absorption spectra. However, the fluorescence was tuneable and determined by the

number of polar solvent molecules in close proximity to the **IFO** molecule.¹⁵ As shown in Fig. 3a, upon gradual addition of DMF into *p*-xylene, the low-energy fluorescent band at 610 nm was progressively decreased along with the increase of high-energy fluorescent band at 436 nm. Strikingly, when the ratio of DMF : *p*-xylene was tuned to 1 : 4 (v/v), white emission was obtained with CIE of (0.35, 0.32) as shown in Fig. 3b.¹⁶

Additionally, such multicolour emission can be achieved when **IFO** encounters with surrounding polymer matrixes having different polarities (Fig. 4 and S9[†]).¹⁷ Polysulfone (PSF) and polystyrene (PS) were chosen as host polymer matrixes to examine fluorescent properties. The **IFO** doped PS and PSF films were fabricated by using drop casting from a chloroform (CHCl₃) solution containing **IFO** (1 wt%) onto the surface of quartz cells. The low doping level ensured that **IFO** was molecularly dispersed into polymer matrixes without the formation of aggregates. The emission spectra and photographic images of **IFO**-doped-PS and -PSF films were shown in Fig. 4. The emission colours are identical to those observed in solution. The fluorescent maximum of **IFO** embedded in PS is

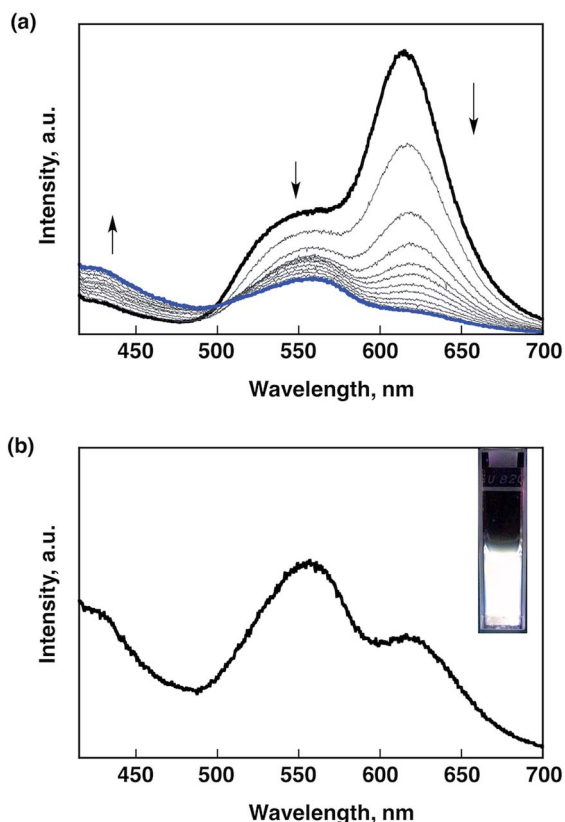


Fig. 3 (a) Fluorescence spectral change of **IFO** (20 μ M) in binary solvents system (DMF and *p*-xylene) in the presence of 0% DMF (black line) to 50% DMF (blue line). Excitation wavelength is 355 nm. (b) White light emission of **IFO** in binary solvent system with DMF : *p*-xylene = 1 : 4 (v/v). Inset: a photograph under irradiation with 365 nm UV-lamp.

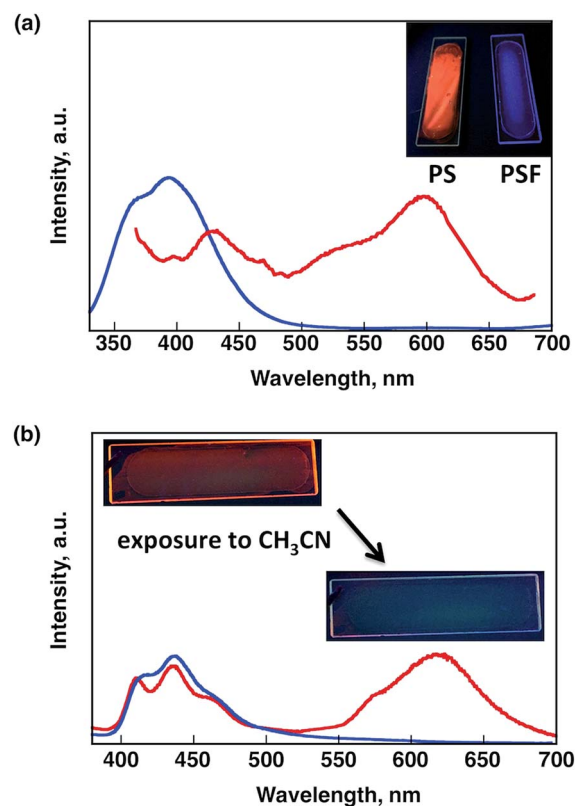


Fig. 4 Fluorescence spectra of **IFO** doped in PS (red line) and PSF (blue line) as host matrixes fabricated by drop casting of CHCl₃ solution containing the corresponding **IFO** (1 wt%). Excitation wavelength is 315 nm for PSF film and 355 nm for PS film. Inset: corresponding photographs under irradiation with UV-lamp. (b) Fluorescence spectral change of **IFO** doped PS film before (red line) and after exposure to acetonitrile (blue line), excitation wavelength is 355 nm. Inset: corresponding fluorescent images of **IFO** doped PS films before and after acetonitrile exposure.

located at 598 nm, showing red emissive colour with CIE of (0.23, 0.20). While the polymer matrix changed to PSF, the emission maximum is dramatically hypsochromic shifted to 393 nm exhibiting blue emission with CIE of (0.31, 0.25). This result indicates that **IFO** exhibits high sensitivity towards microenvironments surrounding **IFO** molecule.¹⁸ We further utilized the **IFO**-doped PS film to study the feasibility of selective detection of common organic solvents, in which **IFO** is able to act as an indicator. The organic solvents were placed onto **IFO** embedded PS film and resulting luminescent colour change was monitored after 10 min. The **IFO**-doped PS film showed distinct colour change from red to blue upon exposure to acetonitrile, ethyl acetate and methanol probably because of large polarity of solvents permeating into PS matrix. In contrast to the above, no visible response towards MCH, DCM, CHCl₃, THF and toluene was observed (Fig. 4b). Such discriminated colour response was reversibly observed upon exposure and evaporation of the above solvents.

In conclusion, we have successfully demonstrated that a newly designed D–A–D fluorophore, **IFO**, presented multiple fluorescence channels that can be switched depending on micro-environmental polarity such as solvent and polymer matrix. We believe that our molecular design would help and extend the limited design concept of ICT molecules towards stimuli-responsive and full-colour emissive materials.

Note added after first publication

This article replaces the version published on 31st August 2016, in which the data in Table 1 were incorrectly grouped through editorial error.

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- 18 Similarly, **FO** also exhibits the tunable emissions when doped in PSF and PS polymer matrixes (Fig. S10 and S11†).