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Solvatochromic and Solid-State Emissive Azlactone-Based AIEE-Active Organic Dye: Synthesis, Photophysical Properties and Color-Conversion LED Application

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Abstract

Here, we report one-pot synthesis of a new azlactone-based dye bearing isoxazole moiety as a donor group (i.e., Dye-Iso), which displays fluorescence emission both in solution and solidstate, and a systematic study of its photophysical properties. The analyses of steady-state photoluminescence (PL) spectroscopy measurements reveal that Dye-Iso exhibits positive solvatochromic behavior accompanied by the decreasing trend in PL quantum yield (QY), as the polarity of solvent increases. In addition, time-resolved fluorescence (TRF) spectroscopy shows that the PL lifetime is shortening and overall effective nonradiative decay rate becomes accelerated with increasing polarity of the medium, which explain well the decrease in PL QY. These findings strongly suggest that the dipole-dipole interactions between the dye molecule having intramolecular charge transfer (ICT) characteristic and solvent are responsible for the redshift in PL emission with the increase in solvent polarity. Furthermore, the electronically ground- and excited-state dipole moments were determined by using linear correlation methods having different solvent polarity functions. The results depict that the Dye-Iso has a larger excited-state dipole moment as against that in the ground-state, which reflects the ICT mechanism. The spectroscopic studies show that the Dye-Iso exhibits aggregation-induced emission enhancement (AIEE) under aggregate formation and is AIEE-active compound. The PL QYs of the Dye-Iso in aggregation- and solid-state were also found to be higher in comparison with those in solutions, which has been elucidated by the increase in the radiative decay rate due to reduced restriction of intramolecular motions (RIM). Finally, we have demonstrated that the AIEE-active Dye-Iso can be used as a color-conversion material for solid-state lighting applications by employing that on a commercial near-ultraviolet LED.

KEYWORDS: Azlactone, solvatochromic fluorescence, intramolecular charge transfer, aggregation-induced emission enhancement, solid-state emission, dipole moment

Introduction

Fluorescent organic compounds from past to date are always one of the most studied optical material groups having considerable interest due to their photophysical properties as well as some advantages like easy synthesis, low cost and toxicity [1,2]. Their fluorescence emission kinetics are typically governed by electronic transition delocalized over the whole chromophore under photoexcitation in conventional organic dyes such as rhodamine and fluorescein, whereas it is originated from intramolecular charge transfer transitions (ICT) in the fluorescent compounds comprising electron-donating and -accepting groups [3–5]. The charge-separated structure provides tunable photophysical properties such as spectral positions, fluorescence quantum yield and lifetime with structural modification of the attached donor and acceptor groups [6–11]. In addition, their photophysical properties are affected by environmental parameters such as viscosity [12,13] and polarity [8,14] due to the redistribution of charges in the excited state under optical excitation, which makes them well environment probe [15,16].

Although organic fluorescence materials display well fluorescence emission in their dilute solutions, they suffer from the solid states such as crystals and thin films in which emission either decreases or completely disappears due to the molecular aggregation, which is called as aggregation-caused quenching (ACQ) [17,18]. This phenomenon generally originates from strong intermolecular interactions (e.g., π - π stacking) that favors the nonradiative relaxation processes [19,20]. However, in practice, this is an undesirable and problematic condition to

incorporate the fluorescent organic materials especially into optoelectronic and biological applications that require the aggregate or solid molecular ensemble [21–24]. Therefore, overcoming the ACQ effect in the solid phase of fluorescent organic materials is crucial, and in the literature, there are extensive studies to reduce or suppress this effect and develop the solid-state emissive organic material [25–27]. Early in the 2000s, Tang et al. reported an unusual phenomenon with a series of studies based on π -conjugated organic compounds displaying emission in solid-state but not in solution. The phenomenon is called aggregation-induced emission (AIE), which is generally explained by restriction of intramolecular motions (RIM) that includes intramolecular rotations and vibrations [28–31]. Based on this result, the color modulation of the emission in the solid phases of some functionalized boron diiminates has been also reported with unique optical properties [32].

Furthermore, the development of new organic compounds exhibiting fluorescence emissions, both in dilute solution and solid-state, has attracted much attention and it is still a challenge [33–36]. For instance, it was shown that a covalently modified anthracene derivative exhibits persistent and strong blue emission in both solution and solid phases [35]. In another study, fluorine-containing diphenylacetylenes having extended π -conjugated structure with a large molecular dipole moment have been demonstrated as alternative candidates for organic molecules exhibiting fluorescence characteristic both in the solid-state and their dilute solutions [36]. Recently, Lu and co-workers have reported a series of triazolopyridine–thiophene donor–acceptor–donor (D–A–D) type conjugated molecules with PL QYs reaching 89% in solution and 29% in solid-state [37].

One other candidate structure for organic emitters both in solution and solid phases is the azlactone (or oxazolone) derivates are known as notable intermediates and modified to reach

synthetically valuable heterocycles over the past decades [38]. These heterocycles not only exhibit various biological activities [39] but also display promising photophysical and chemical sensor properties [40,41], leading an increased interest for the development of new azlactone compounds.. For instance, when the substituent on para-position of phenyl ring of azlactone is an electron-donating one, such as OCH₃ and N(CH₃)₂, it has been reported that they exhibit remarkable photophysical properties as molecular photoswitches [42,43], a green fluorescent protein chromophore [44] and an optical sensor for pH measurements [40]. In addition, the azlactone derivatives have been also noticed as highly emissive in polymer matrices compared with their solution phases [40,45,46]. However, a very limited number of studies have been published associated with azlactone derivatives displaying fluorescence emission both in liquid and solid phases, and to the best of our knowledge, no study including an application utilizing their solid-state fluorescence properties have been reported to date.

To this end, here we designed and synthesized a new azlactone-based molecule (i.e., Dye-Iso), which displays fluorescence properties both in solution and solid-state, by positioning the heterocyclic aromatic isoxazole as an electron-donating group on the 4-position of the azlactone ring. The structural and photophysical properties of the fluorescent Dye-Iso were systematically investigated by using infrared (IR), nuclear magnetic resonance (NMR), mass (MS), UV-Vis absorption, steady-state photoluminescence (PL) and time-resolved fluorescence (TRF) spectroscopy. The strong solvent polarity dependent fluorescence behavior (i.e., bathochromic shift) and the decrease in PL QY were simultaneously observed with increasing solvent polarity. In addition, the significant shortening in fluorescence decay lifetime and acceleration in the nonradiative decay rate with increasing medium polarity reveal the ICT character of the fluorophore. The ICT characteristic of the Dye-Iso was also analyzed by different

solvatochromic shift methods, which strongly suggest the excited-state dipole moment of the fluorophore is greater than that of the ground-state. Besides, in aggregation state, the Dye-Iso has displayed aggregation-induced emission enhancement (AIEE) in acetone/water mixture. Besides, it was found that the PL QY of the Dye-Iso in the solid-state is higher than those in the solution ones, which can be explained by restriction of intramolecular motion (RIM). The achieved promising photophysical properties in solid-state can make this organic compound a suitable candidate for solid-state lighting applications. With this motivation, as a proof-of-concept demonstration, we employed the synthesized Dye-Iso compound as a color-converter material on a light-emitting diode (LED).

Results and Discussion

The synthesis of fluorescent azlactone-based dye (i.e., Dye-Iso) was carried out using the traditional Erlenmeyer-Plöchazlactone method. Figure 1 shows the molecular structure and synthetic routes of target Dye-Iso molecule. Briefly, first, 1,3 dipolar cycloaddition reaction of nitrile oxide formed in situ by the oxidation of p-(methoxy)benzaldoxime **1** with NaOCl to propargyl alcohol **2** gave isoxazole substituted methanol **3** in a regioselective manner. Then, it was readily oxidized to its corresponding aldehyde **4**, key intermediate precursor, by pyridinium chloro chromate (PCC) in good yield. Finally, acetic anhydride mediated condensation of hippuric acid **5** with heterocyclic aldehyde **4** yielded only *E* isomer of target fluorescent molecule (Dye-Iso) in one pot (see Figure 1b). Structural elucidation of all precursors and Dye-Iso were performed by IR, NMR, Mass data and physical characteristics, i.e., melting point, (see experimental section for details).



Figure 1. (a) 4-isoxazole substituted oxazol-5(4H)-one (Dye-Iso). (b) Synthetic pathway of the Dye-Iso.

Figure 2 depicts the UV-Visible absorption and steady-state photoluminescence (PL) emission profile of the Dye-Iso dissolved in some aprotic solvents having different polarities, and all photophysical properties are summarized in Table 1. All the measurements were performed at room temperature. As can be seen in the absorption spectra (Figure 2a), the two main absorption peaks have emerged for each dye solution having different polarity, where the first absorption maximum is positioned between 263 and 265 nm, whereas the second one having the highest absorbance is centered between 365 and 370 nm at the lower-energy side of the spectrum. In addition, the shape of the absorption band of the Dye-Iso remains almost unchanged with the increasing solvent polarity although position of that changes with slight redshift of a few nanometers. As seen in the inset of Figure 2a, the maximum spectral shifts in the main absorption peaks were found to be 2 and 5 nm for the higher- and lower-energy sides of the spectrum, respectively, with increasing solvent polarity. This nearly solvent polarity independent behavior in the absorption spectra indicates that the ground-state of the dye is not affected dramatically in the mean of structural and electronic properties with increasing solvent polarity [47]. To better analyze the absorption behavior of the Dye-Iso, the density functional theory (DFT) and the time-dependent density functional theory (TD-DFT) calculations were carried out

by using Gaussian 09W software [48]. The hybrid exchange-correlation B3LYP functional with the 6-311G(d) basis set was employed during the calculations [49,50]. Figure 2b shows the localizations of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) on the optimized structure of the Dye-Iso for the gas phase. The HOMO density is mainly localized on the isoxazole moiety with bearing phenyl ring, whereas LUMO density is mainly located on the azlactone moiety. The energies of HOMO and LUMO are associated with the ionization potential and the electron affinity of a molecule, respectively. Hence, the HOMO and LUMO localizations on the Dye-Iso molecule depict that the isoxazole and azlactone moieties have the ability to donate and accept electrons, respectively, and indicate the intramolecular charge transfer (ICT) character of the Dye-Iso. The computed UV-Vis spectra of the Dye-Iso for different solvent mediums are also represented in Figure 2c. The absorption maxima at the higher-energy side of the spectrum were located between 258 and 260 nm, whereas the dominant absorption maxima were found to emerge between 397 and 399 in the computed absorption bands for different solvents. The results show that the simulated absorption bands were in very close agreement with the experimentally obtained ones. In addition, according to the results of the TD-DFT calculations performed for the gas phase (see Figure S8), the dominant absorption band was found to correspond to HOMO-1 \rightarrow LUMO transition having 94.20 % contribution with the oscillator strength of 1.1396 and had an ICT character. The computed parameters characterizing the absorption features of the Dye-Iso, such as excitation energy, wavelength, oscillator strength, and the major component in terms of the percentage contribution of the molecular orbital transitions are summarized in Table S2 (see supporting information).



Figure 2. (a) UV-Vis absorption spectra of the Dye-Iso in solvents having different polarity. (b) Localizations of the HOMO and LUMO on the optimized structure. (c) Computed UV-Vis absorption spectra of the Dye-Iso in solvents having different polarity employing TD-DFT calculation. (d) Normalized photoluminescence spectra of the Dye-Iso in solvents having different polarity. The inset in (a) and (c) show the zoom-in of the normalized curves belonging to same absorption data. DCM and DCE are represent the abbreviation for solvents of Dichloromethane and 1,2-Dichloroethane, respectively.

On the other hand, the PL emission spectrum of the Dye-Iso exhibits significant solvent polarity dependent behavior contrary to its absorption spectrum (see Figure 2b). All the steady-state PL measurements were carried out under the excitation at 375 nm by a continuous-wave pump. As the polarity of solvent is increased, the PL emission maximum of the Dye-Iso shifts to the longer wavelength of the spectrum (i.e., bathochromic shift). The maximum shift in the peak position of PL emission due to solvent polarity was found to be ~62 nm (i.e., from 510 nm in 1,4-dioxane to

572 nm in 1,2-dicholoraethane). Owing to the nearly unchanged absorption features despite the strong change in the PL emission profiles with the increase in solvent polarity, the Stokes shift in a polar solvent is larger than that in relatively non-polar solvent (see Table 1). It is well known that the intermolecular interactions between the solute and solvent molecules can affect some photophysical properties of the environment-sensitive molecules such as absorption and fluorescence features via hydrogen bonds and dipole-dipole interactions [51]. Here, the observed bathochromic behavior, or positive solvatochromism, in the PL emission curve with increasing polarity can be elucidated to dipole-dipole interactions between the dye and the host, due to the fact that aprotic solvents cannot make any hydrogen bonding with the dye. The redshifted PL behavior indicates the excited-state dipole moment (μ_e) of the Dye-Iso is larger than that in its ground state (μ_g), owing to redistributed charge separation under excitation between the electron-donating isoxazole ring and the electron-accepting azlactone ring (i.e., intramolecular charge transfer, ICT). Therefore, this is resulted with lowering in excited state energy of the Dye-Iso, inducing from rotationally re-oriented solvent molecules surrounding the dye [52].

In order to deeply analyze the effect of solvent polarity on the fluorescence properties of the Dye-Iso, the PL QY measurements were also conducted. Here, the de Mello methodology [53] was utilized to determine the PL QYs of the Dye-Iso for different solvent media, and all the measurements were carried out using a calibrated integrating sphere at 375 nm excitation. During the measurements, dilute solutions of the dye were studied to eliminate the probability of re-absorption effect. The evolution of the PL QY of the Dye-Iso as a function of the solvent polarity is given in Figure 3a. The PL QY of the Dye-Iso exhibits decreasing trend with increasing solvent polarity. The highest value for the PL QY was found to be 40.5% in 1,4-dioxane, whereas it decreases down to 12.6% in 1,2-dicholoraethane (see Table 1). This significant

change in PL QY clearly indicates the solvent polarity dependence of fluorescence mechanism of the Dye-Iso, and a change in the nonradiative decay rate can be responsible for the decrease in the PL QY.

Table 1. Photophysical properties of the Dye-Iso in different aprotic solvents at room temperature as a function of the solvent polarity scale of $E_T(30)$.

Solvent	$E_T(30)^{\rm a}$	$\lambda_a{}^{\mathrm{b}}$	ε°	λ_{PL}^{d}	fwhm ^e	$\Delta\lambda^{f}$	$oldsymbol{\phi}^{ \mathrm{g}}$	τ^{h}	k_r^{i}	k_{nr}^{j}
		(nm)	$(x10^4 M^{-1} cm^{-1})$	(nm)	(nm)	(nm)	(%)	(ns)	x10 ⁷ (s ⁻¹)	x10 ⁷ (s ⁻¹)
Dioxane	36.0	263 / 365	1.03 / 2.62	510	132.01	145	40.5	7.96	5.09	7.47
Chloroform	39.1	264 / 368	1.15 / 1.92	529	137.31	161	29.4	6.22	4.73	11.35
DCM	40.7	265 / 369	0.98 / 1.90	561	164.75	192	21.7	5.22	4.15	14.94
DCE	41.3	265 / 370	1.04 / 2.00	572	165.73	202	12.6	4.83	2.62	18.09

^a The solvent polarity scales [16].^b Absorption maxima for two main peaks. ^c Molar extinction coefficients (absorptivities) for two main peaks. ^d Photoluminescence maxima. ^e Full-width half-maximum of the PL emission peak. ^f Stokes shift according to the dominant absorption peak. ^g Photoluminescence quantum yield. ^h Fluorescence lifetime, ⁱ Radiative decay rate, ^j Nonradiative decay rate. DCM and DCE are represent the abbreviations for solvents of Dichloromethane and 1,2-Dichloroethane, respectively.

To better understand the underlying reason in decreased PL QY with increasing solvent polarity, time-resolved fluorescence (TRF) measurements were also carried out using the time-correlated single photon counting system with picosecond pulsed-pump laser at 375 nm. All the fluorescence decay curves for different solvent medium were collected at the maximum emission wavelength of the Dye-Iso in corresponding solvent. Figure 3b depicts the fluorescence decay profiles of the Dye-Iso in solvents with different polarity. As it is seen from Figure 3b, fluorescence decay curves become faster as the solvent polarity increases. This accelerated decay behavior is a significant indication that overall nonradiative decay pathways could be more dominated with increasing polarity as the decreasing PL QY trend is also considered. In order to analyze the fluorescence decay curves, the data were numerically fitted by using following single-exponential decay function [51],

$$FL(t) = Ae^{-t/\tau} \tag{1}$$

where A and τ are the amplitude of the exponential decay and the fluorescence lifetime, respectively. The obtained fluorescence lifetimes are represented in Figure 3c as a function solvent polarity and summarized in Table 1. It is clearly seen that the fluorescence lifetime of the Dye-Iso exhibits strong solvent polarity dependent behavior. As the solvent polarity is increased, the fluorescence decay lifetime was found to be decreased from 7.96 (1,4-dioxane) to 4.82 ns (1,2-dicholoraethane). In addition, the radiative and nonradiative decay rates of the Dye-Iso for all solvents were analyzed using the fitted fluorescence decay parameters and the PL QYs. The decay rates were computed by the following relations [51],

$$k_r = \frac{\phi}{\tau} \tag{2}$$

and

$$k_{nr} = (1 - \phi)/\tau \tag{3}$$

where k_r , k_{nr} , ϕ and τ are the radiative and nonradiative decay rate constants, PL QY and fluorescence lifetime, respectively. Figure 3d represents the radiative and nonradiative decay rates as a function of solvent polarity. As seen in Figure 3d, an increase in solvent polarity results in a decrease in the radiative decay rate whereas an increase in the nonradiative decay rate. The increasing trend in the nonradiative decay rate with the increasing solvent polarity is an indication to the decreasing behavior in the PL QY of the Dye-Iso. The interaction between solute having ICT characteristic and solvent becomes generally more prominent with increasing solvent polarity. This would feed the nonradiative decay processes and gives rise to a decrease in the PL QY. Therefore, the further increase of nonradiative processes in the fluorescence mechanism of Dye-Iso with increasing solvent polarity can be attributed to the ICT processes [54–56].



Figure 3. (a) Evolution of the photoluminescence quantum yields (PL QY) of the Dye-Iso in different solvent medium. (b) Time-resolved fluorescence decays, (c) fluorescence lifetimes and (d) decay rates of the Dye-Iso as a function of $E_T(30)$ solvent polarity scale. The inset in (b) shows the zoom-in of the same decay curves. The dotted lines are a guide for the eyes.

In order to investigate the solvatochromic behavior of the Dye-Iso, the Stokes shifts between the absorption and fluorescence spectra were analyzed by using linear correlation methods having different orientation polarizability functions proposed by Lippert–Mataga [57,58], Bakhshiev [59], Kawski–Chamma–Viallet [60,61]. The methods, which are most accepted and used techniques in the literature, also enable to estimate the ground- and excited-state dipole moments of the Dye-Iso as well as change between them. The three independent linear correlation equations proposed by Lippert–Mataga, Bakhshiev, Kawski–Chamma–Viallet are given respectively as follow,

$$\bar{v}_a - \bar{v}_f = m_1 f_1(\varepsilon, n) + b_1 \tag{4}$$

$$\bar{v}_a - \bar{v}_f = m_2 f_2(\varepsilon, n) + b_2 \tag{5}$$

$$\frac{\overline{v}_a + \overline{v}_f}{2} = -m_3 f_3(\varepsilon, n) + b_3 \tag{6}$$

where \bar{v}_a and \bar{v}_f are wavenumbers of absorption and fluorescence maximums in cm⁻¹, respectively. The $f(\varepsilon, n)$, $f_2(\varepsilon, n)$ and $f_3(\varepsilon, n)$ characterize the orientation polarizability functions corresponding to related methods. The polarity functions are as follows,

$$f_1(\varepsilon, n) = \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right] \tag{7}$$

$$f_2(\varepsilon, n) = \left[\frac{2n^2 + 1}{n^2 + 2}\right] \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right]$$
(8)

$$f_3(\varepsilon, n) = \left[\frac{2n^2 + 1}{2(n^2 + 2)}\right] \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] + \left[\frac{3}{2}\frac{(n^4 - 1)}{(n^2 + 2)^2}\right]$$
(9)

where the ε and n are the dielectric constant and refractive index of solvent, respectively. The computed polarizability functions for each method are given in Table 2. The m_1 , m_2 and m_3 in the equations given above define the slopes of $(\bar{v}_a - \bar{v}_f)$ vs $F_1(\varepsilon, n)$, $(\bar{v}_a - \bar{v}_f)$ vs $F_2(\varepsilon, n)$ and $\frac{1}{2}(\bar{v}_a + \bar{v}_f)$ vs $F_3(\varepsilon, n)$ graphs represented in Figure 4, respectively and are given as follows

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \tag{10}$$

$$m_2 = \frac{2(\mu_e - \mu_g)^2}{hca^3}$$
(11)

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$$m_3 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \tag{12}$$

Here, the *h*, *c* and *a* are Planck's constant, speed of light in vacuum and Onsager cavity radius, respectively. In this study, the dielectric constants and the refractive indices of the solvents were taken from the literature [11,62], whereas the Onsager cavity radius of the molecule was theoretically determined as 5.61 Å by using density functional theory (DFT-B3LYP/6-311G(d)) calculation.

	Solvents				
-	1,4-Dioxane	Chloroform	DCM	DCE	
ε ^a	2.22	4.81	9.08	10.42	
n ^b	1.4224	1.4454	1.4241	1.4448	
$\bar{v}_a (\text{cm}^{-1})^c$	27397.26	27173.91	27100.27	27027.03	
\bar{v}_f (cm ⁻¹) ^d	19607.84	18903.59	17825.31	17482.52	
$ar{v}_a - ar{v}_f{}^e$	7789.42	8270.32	9274.96	9544.51	
$\frac{1}{2}(\bar{v}_a + \bar{v}_f)(\text{cm}^{-1})^{f}$	23502.55	23038.75	22462.79	22254.77	
$f_1(\varepsilon, n)^{g}$	0.02150	0.14842	0.21838	0.22118	
$f_2(\varepsilon,n)^h$	0.04361	0.37201	0.59500	0.62341	
$f_3(\varepsilon,n)^i$	0.30848	0.48742	0.58529	0.61314	
$f_4(\varepsilon,n)^j$	0.12288	0.25359	0.32005	0.32625	
$f_{\tau}(\varepsilon, n)^{k}$	0.16193	0.42629	0.60163	0.62543	

Table 2. Room temperature spectroscopic properties of the Dye-Iso and the solvent polarity functions for different solvatochromic methods.

^a Dielectric constant. ^b Refractive index. ^c Absorption maxima. ^d Fluorescence maxima. ^e Stokes shift. ^f Arithmetic mean of absorption and fluorescence maximum. ^g Lippert-Mataga solvent polarity functions. ^h Bakhshiev solvent polarity functions. ⁱ Kawski–Chamma–Viallet solvent polarity functions. ^j Weller solvent polarity functions. ^k Retting solvent polarity function.

Figures 4a and 4b depict the variation of Stokes shift as a function of solvent polarity functions proposed by Lippert–Mataga and Bakhshiev. The data were fitted to a straight line and all the fitting parameters are given in Table 3. The data show the linear behavior with correlation coefficients of 0.809 and 0.873 for Lippert–Mataga's and Bakhshiev's plots, respectively. The deviation in the linearity might be related to the specific interactions between the solute and the solvents. The change between the ground- and excited-state dipole moments ($\Delta\mu$) was calculated

by utilizing the slope of the Lippert–Mataga's plot and found to be 12.04D. In addition, the variation of arithmetic means of the Stokes shift as a function of solvent polarity function proposed by Kawski–Chamma–Viallet is represented in Figure 4c. The data exhibit good linearity with correlation coefficients of 0.925.

 Table 3. The calculated fitting parameters and correlation coefficients for different solvatochromic models.

	Slope	Intercept	Correlation coefficient
Method	$m (\mathrm{cm}^{-1})$	$b (\rm cm^{-1})$	R^2
Lippert-Mataga	8268.86	7459.86	0.809
Bakhshiev	2955.14	7512.60	0.873
Kawski–Chamma–Viallet	4005.19	24811.64	0.925
Weller	9834.33	20969.38	0.852
Retting	4435.68	20467.83	0.910

Utilizing the slopes of the Bakhshiev and the Kawski–Chamma–Viallet plots, the ground- (μ_g) and excited-state (μ_e) dipole moments were also estimated. To this end, the following equations can be derived using equations (11) and (12) in the case of assumptions that the solute geometry does not change during the electronic transition and electric dipole moments (i.e., μ_g and μ_e) are in parallel [11].

$$\mu_g = \frac{(m_3 - m_2)}{2} \sqrt{\frac{hca^3}{2m_2}}$$
(13)

$$\mu_e = \frac{(m_3 + m_2)}{2} \sqrt{\frac{hca^3}{2m_2}} \tag{14}$$

$$\mu_e = \left[\frac{m_3 + m_2}{m_3 - m_2}\right] \mu_g \text{ for } m_3 > m_2 \tag{15}$$

The ground- (μ_g) and excited-state (μ_e) dipole moments were found to be 1.29D and 8.49D, respectively, using the equations (13) and (14). The ratio of the ground- and excited-state dipole moments (μ_e/μ_g) was also estimated as 6.59. The findings support the observed spectral shift in

PL emission with increasing solvent polarity and strongly indicate that redistribution of the charge densities in the excited-state is the main responsible mechanism for the large difference between the μ_g and μ_e . This makes the excited-state more polar than the ground-state and it is also a reflection of the ICT mechanism as well [8]. However, owing to the fact that the emission arising from the charge transfer state (CTS) is not attainable by direct excitation and the absorption characteristic of the CTS is not known, the excited-state CT characteristic of the Dye-Iso was also analyzed by Weller's method [52,63]. The equation, which only associated with the shift in emission spectrum, proposed by Weller is as follows.

$$\bar{v}_f = -m_4 f_4(\varepsilon, n) + b_4 \tag{16}$$

$$f_4(\varepsilon, n) = \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{4n^2 + 2}\right] \tag{17}$$

$$m_4 = \frac{2\mu_e^2}{hca^3} \tag{18}$$

Figure 4d shows Weller's plot with a linear regression coefficient of 0.852 and indicates the excited-state ICT characteristic of dye. The excited-state dipole moment of the Dye-Iso was also estimated by using the slope of the Weller's plot and found to be 13.13D.

Table 4. Ground- and excited-state dipole moments of the Dye-Iso. $\Delta \mu(D)^a$ $\mu_g(D)^b$ $\mu_e(D)^c$ μ_e/μ_g^d $\mu_e(D)^e$ $\mu_e(D)^f$ 12.041.298.496.5913.138.82

^a The change in dipole moment calculated from Equation (10). ^b The ground-state dipole moment calculated from Equation (13). ^c The excited-state dipole moment calculated from Equation (14). ^d The ratio of excited-state dipole moment and ground-state dipole moment calculated from Equation (15). ^e The excited-state dipole moment calculated from Equation (15). ^f The excited-state dipole moment calculated from Equation (21). In the calculations, 1 Debye was taken as 3.33564×10^{-30} cm.

The large change in electric dipole moments between the ground- and excited-states is a direct indication of the ICT characteristic and points to the possible existence of another mechanism known as twisted intramolecular charge transfer (TICT) originated from structural conformation. Therefore, the TICT characteristic of the dye was analyzed by utilizing Retting method [52,64]. The Retting's equation is as follows,

$$\bar{v}_f = -m_5 f_5(\varepsilon, n) + b_5 \tag{19}$$

$$f_5(\varepsilon, n) = \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{2n^2 + 4}\right] \tag{20}$$

$$m_5 = \frac{2\mu_e^2}{hca^3} \tag{21}$$

Figure 4e represents the Retting's plot and the data show good linearity with a correlation coefficient of 0.910. This suggests that the redshift in the PL emission spectrum with the large Stokes shift might be predominantly associated with the TICT process. With increasing solvent polarity, the broadening in full-width half-maximum (fwhm) of the PL emission band (see Table1), the large Stoke shift, the decreasing PL QY and the large change between the ground-and excited-states dipole moments strongly point out the TICT mechanism in the Dye-Iso [65]. The excited-state dipole moment of the Dye-Iso was also found to be 8.83D by using the slope of the Retting's plot.



Figure 4. Solvatochromic linear plots of the Dye-Iso as a function of (a) Lippert-Mataga, (b) Bakhshiev, (c) Kawski–Chamma–Viallet, (d) Weller and (e) Retting solvent polarity functions. The dotted lines show the corresponding linear fittings.

To understand the Dye-Iso is whether AIE-active or not, the effect of aggregation on its fluorescence behavior was also investigated. To this end, a series of colloidal suspensions was prepared using acetone and Milli-Q water, where the Dye-Iso is dissolved well in acetone, whereas it is insoluble in water. The aggregation experiment was carried out by varying the fractional ratios of water in the colloidal suspensions, where the existing form of the Dye-Iso molecules can be changed with increasing water fraction from solution to aggregation state. The concentration of the all suspensions were kept in 5.0×10^{-5} M during the measurements. Figure 5a depicts the UV-Vis absorption spectra of the Dye-Iso in varying volume to volume (v/v) ratio of acetone/water mixtures. The inset in Figure 5a also shows the molar extinction coefficients (absorptivities) of the mixtures corresponding to 365 nm and summarized in Table S2 (see supporting information). As can be seen in Figure 5a, with increasing content of water in the mixture, up to 60%, no dramatic change is observed in the absorptivity of the mixture, whereas it is significantly decreased between 70 and 95% of water content. The decrease in absorptivity with the further increase of water fraction in acetone/water mixture is an indication of aggregate

formation resulting from the degraded solvating power of the aqueous mixture. In addition, an increase in the tails of absorption curves after 70% water fraction is started to appear. In literature, such tails have been observed, which originates from the formation of nano-aggregates in colloidal suspensions comprising organic systems with different water fractions, and they are explained by Mie scattering [66,67]. Furthermore, the PL spectroscopy measurements were carried out to investigate the emission characteristic of the Dye-Iso in the aggregation phase. Figure 5b shows the PL emission spectra of the Dye-Iso as a function of the acetone/water ratio (v/v) in the mixture. The Dye-Iso exhibits very weak fluorescence emission in dry acetone at about 573 nm because of the strongly polarized ICT state. However, due to the polarity of medium is increased with the addition of an amount of water, the ICT effect becomes more prominent that enables nonradiative decay processes. Therefore, it is observed that the PL emission is quenched up to 4:6 v/v ratio of acetone/water. In this case, the molecular dissolution of the Dye-Iso can continue through still sufficient solvation power of the acetone/water mixture. With the further increase in water fraction, AIE characteristic have been started to be observed in the PL emission spectrum. The PL spectra exhibit blue-shifted behavior with a gradually enhanced PL maxima as the water fraction increases and it reaches the maximum level in the suspension comprising 95% of water. The enhancement in PL emission accompanied by a blueshifting emission maximum can be attributed to the limitation of ICT effect. The evolution of the PL maxima with increasing water content is depicted in Figure 5c. In addition, to have a better insight into the increase in the emission characteristic of the Dye-Iso, the PL QY measurements were performed (Figure 5d). It was found that the PL QY was in the tendency to an increase, where the PL QYs were found to be 12.9, 18.9, and 54.1 % for water fraction of 80, 90, and 95



% in the mixtures, respectively. These results reveal that the Dye-Iso displays aggregationinduced emission enhancement (AIEE) characteristics and it is an AIEE-active compound.

Figure 5. (a) UV-Vis absorption and (b) photoluminescence spectra of the Dye-Iso in varying volume to volume ratio of acetone/water mixtures. Evolution of (c) the photoluminescence emission maxima and (d) photoluminescence quantum yield of the Dye-Iso as a function of water fraction in the mixtures. The insets in (c) are the images of the Dye-Iso dissolved in solvent mixtures having different water content under day-light and UV-illumination with a 365 nm UV-lamp. The red dashed line in (b) shows the zeropoint, whereas the black dotted lines are a guide for the eyes.

Furthermore, the Dye-Iso not only exhibit fluorescence emission in solution but also in solidstate. Figure 5a shows the PL emission profile of the Dye-Iso in the solid-state under 405 nm excitation and the data were collected via Ocean Optics spectrometer. In the case of the solidstate, the shape of the PL emission band exhibit slight change, and the nearly symmetric behavior of the emission in solution phases is disappeared. The shape of the PL emission in

mechanofluorochromic (MFC) materials typically depends on the aggregation condition in the solid-state [68]. Therefore, the change in the shape of the PL emission profile can be an indication for the MFC behavior in the solid phase of the sample. The PL emission maximum in the solid-state is located at 527 nm and exhibits a shift to the lower energy side of the spectrum as compared to that of its solution form in 1,4-Dioxane (i.e., 510 nm). Besides, the PL emission band in the solid-state becomes narrower (i.e., fwhm~101.37 nm) than those in solutions (see Table 1). The redshifting and narrowing behaviors in the emission line of the Dye-Iso is an indication of the AIE characteristic govern by formation of aggregates in solid form [69]. These spectral changes in the emission spectrum are due to possible specific molecular interactions, such as intermolecular stacking and π - π interactions, caused by near-field strong dipole-dipole interactions in the solid-state [70]. In the case of the fluorescent organic molecules having planar structure, specific molecular interactions give rise to a decrease in PL QY due to the increasing nonradiative recombination of the excited-state electrons in the aggregate forms of the condensed state [25]. However, in our case, by using the calibrated integrating sphere, the PL QY of the dye in the solid-state was measured to be 61.3% which is high as compared to those in the solutions. The higher PL QY behavior in aggregate- or solid-state than that in solution is a very common property of the AIEE-active chromophores, which is explained by restriction of intramolecular motions (RIM). In solution, the intramolecular motions (i.e., intramolecular rotations and vibrations) such as fast rotation of phenyl rings give rise to dissipate the energy of absorbed photons. This leads to deactivate the radiative relaxation pathways of the excited state electrons and reduces the PL QY. In solid-state, the intramolecular motions are restricted by the physical constraints and results in enhanced PL emission due to the blocking of the nonradiative decay channels. In addition, another proposed mechanism is suppressing intermolecular π - π stacking.

This mechanism also leads to a decrease in the nonradiative decay rate and enhanced the PL QY. To analyze decay kinetics of the excited state electrons in solid-state, time-resolved fluorescence measurement was also performed. Figure 6b represents the fluorescence decay curve of the Dye-Iso in solid-state. The decay curve was numerically fitted by using single-exponential decay function and the fluorescence decay lifetime was found to be 7.78 ns. The radiative and nonradiative decay rate constants were computed as 8.10×10^7 and 4.97×10^7 s⁻¹, respectively. The decrease in the nonradiative decay rate as compared to those in the solutions indicates that restriction of intramolecular motions and suppression of strong intermolecular interactions can be responsible for the increased PL QY in aggregation- and solid-state.

Finally, as a proof of concept demonstration, the Dye-Iso displaying efficient solid-state fluorescence emission was tested as a color-converting material for solid-state lighting applications. To this end, a monolith including the dense Dye-Iso was prepared in a pellet form. In the process, first, the dye in solid was grinded with the KBr salt, which has a large transmission window in the visible and infrared spectra, to get a well-structured monolith and then it was pressed for 10 min under 60 kN. The prepared monolith was employed on a high power near-UV-LED emitting at 405 nm. Figure 6c depicts the spectrum of the resulting dye-monolith with an integrated LED. The emission spectrum of the dye-monolith exhibits redshifted behavior (from 527 to 535 nm) as compared to that of the pristine solid (see Figures 5a and 5c). The redshifted emission resulting from the external mechanical effect implies that the Dye-Iso shows a typical MFC property. The shifts in the solid-state emission peak wavelength can be associated with the change of molecular packing mode as a response to external physical effects (e.g., grinding and pressing) [71,72]. Besides, the solid-state emission line of the Dye-Iso in the form of the monolith shows slight broadening (i.e., *fwhm*~106.81 nm) with respect to that in the

powder form. This spectral broadening of 5.44 nm in the emission band can be ascribed to a change of the dielectric medium surrounding the dye [73] due to KBr. After analyzing the PL emission spectrum of the dye-monolith, in order to the characterize the shade of the monolith integrated LED emission, Commission Internationale de l'Enclairage (CIE) color coordinates (x,y) and correlated color temperature (CCT) of the emission of the monolith integrated LED were determined by using the spectrum given in Figure 6c. The corresponding color coordinates were found to be (0.1716, 0.0087) for the only-near-UV LED and (0.3784, 0.5660) for the dye-monolith integrated LED and they are represented on the CIE 1931 chromaticity diagram in Figure 6d. The CCT value for the dye-monolith integrated LED was also determined as 4780 K. The findings show that the Dye-Iso in solid-state can be used as color-conversion material in solid-state lighting applications.



Figure 6. (a) Normalized photoluminescence spectrum and (b) time-resolved fluorescence decays of the Dye-Iso in solid-state. The insets in (a) and (b) show the photographs of the synthesized dye sample in solid under day-light (left) and UV-excitation (right), and the zoom-in of the same decay curves, respectively. (c) Normalized emission spectrum of the dye-monolith integrated near-UV LED. (d) CIE coordinates of the only-near-UV LED and dye-monolith integrated near-UV LED. The inset in (c) and (d) show the zoom-in of photographs of the dye-monolith under day-light (top) and UV-excitation (right), and dye-monolith integrated near-UV LED, respectively.

Conclusion

In summary, we have described the synthesis and photophysical properties of the Dye-Iso displaying fluorescence emissions both in solution and solid-state. In solution, the systematic steady-state and time-resolved fluorescence studies shows that the fluorescent Dye-Iso exhibits the ICT-based photophysical properties depending on the solvent polarity. The strong redshifted behavior in the PL maximum was observed with the increasing solvent polarity in comparison to that of the absorption, which enable to large Stokes shift of 202 nm in 1,2-Dichloroethane. The

Dye-Iso also shows solvent dependent behavior in the PL QY, and the time-resolved fluorescence analyses indicate that the nonradiative recombination processes become more dominant when the polarity of medium surrounding the dye increases. These findings reveal that an increase in polarity of solvent enables a more prominent dipole-dipole coupling between the solvent and the dye molecules having ICT character. Furthermore, the methodological analyses that are carried out by using linear correlations with different polarity functions show that the excited-state dipole moment is about 6.7-fold higher than that of its ground-state. The higher polarity in the excited-state is an indication for the ICT character of the Dye-Iso. Furthermore, the spectroscopic measurements reveal that the Dye-Iso also exhibits AIEE behavior in its colloidal suspensions containing acetone/water mixture. The PL QY in the solid-state was also found to be increased up to 4.8-fold higher than those in the solutions. The enhancement in the PL QY in aggregation- and solid-state was explained by in terms of the restriction of intramolecular motions in view of the decrease in nonradiative decay rate. Considering the photophysical properties including the high PL QY and large Stoke-shifted emission in the solidstate, the Dye-Iso has become highly promising material for optoelectronic applications. Finally, as a proof-of-concept demonstration, it has been shown that with employing the Dye-Iso on the commercial LED it can be utilized as a color-conversion material for solid-state lighting applications.

EXPERIMENTAL SECTION

General procedure for synthesis of 3-(4-methoxyphenyl)isoxazole-5-carbaldehyde (4):

To a mixture of (3-(4-methoxyphenyl)isoxazol-5-yl)methanol (3) (0.810 g, 4 mmol) in CH₂Cl₂ (25 mL) was added pyridinium chlorochromate (PCC) (2.150 g, 10 mmol) and stirred at room temperature for 24 h. The reaction progress was monitored by TLC. After completion of the reaction, the reaction mixture was washed with water and extracted with CH₂Cl₂ through multiple extractions. The combined organic layers were dried over Na₂SO₄ and evaporated under vacuum to give a crude product which was then purified by column chromatography on silica gel 100 (eluent EtOAc - Petroleum ether 4:1 (v/v) to furnish the desired aldehyde as yellow solid.

3-(4-methoxyphenyl)isoxazole-5-carbaldehyde:

Yellow solid (0.552 g, 68%). m.p. 94-96 °C. IR (KBr): v = 3474, 1697 (C=O), 1616, 1527, 1450, 1301, 1253, 1172, 1028, 916, 831, 744 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.01 (s, 1H), 7.79 (d, J = 8.9 Hz, 2H), 7.22 (s, 1H), 7.00 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H).

General procedure for synthesis of (E)-4-((3-(4-methoxyphenyl)isoxazol-5-yl)methylene)-2phenyloxazol-5(4H)-one (**Dye-Iso**):

A mixture of 3-(4-methoxyphenyl)isoxazole-5-carbaldehyde (4) (0.438 g, 2.16 mmol), hippuric acid (5) (0.440 g, 2.46 mmol), and sodium acetate (0.089 g, 1.08 mmol) in acetic anhydride (0.6 mL) was stirred at 60 °C for 3h. After cooling the solution to room temperature, water (30 mL) was added, and the precipitated crude fluorescent azlactone dye was filtered and washed with cold water. The product was dried under vacuum for several hours and it was recrystallized from acetone.

(E)-4-((3-(4-methoxyphenyl)isoxazol-5-yl)methylene)-2-phenyloxazol-5(4H)-one (**Dye-Iso**):

Yellow solid (0.583 g, 78%). m.p. 160-162 °C. IR (KBr): v = 2922, 2849 (aliphatic CH), 1804 (ester C=O), 1728 (C=N azlactone), 1656 (C=N isoxazole), 1609, 1428, 1248, 1178, 808, 702cm⁻

¹; ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, J = 7.0 Hz, 2H), 7.85 (d, J = 8.6 Hz, 2H), 7.68 (t, J = 6.9 Hz, 1H), 7.59 – 7.55 (m, 3H), 7.23 (s, 1H), 7.01 (d, J = 8.7 Hz, 2H), 3.87 (s, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 165.90, 165.05, 163.02, 161.33, 158.03, 136.18, 134.52, 129.26, 129.06, 128.56, 128.48, 124.86, 114.49, 114.01, 107.38, 55.50; HRMS (+APCl) calcd for C₂₀H₁₅N₂O₄ [M+H]⁺ 347.1032, found 347.1035.

ASSOCIATED CONTENT

Supporting Information

Infrared (IR), Nuclear Magnetic Resonance (NMR), Time-of-flight mass spectrometry (TOF-MS) data, computed IR and UV-Vis spectra for gas phase using DFT and TD-DFT calculations. AUTHOR INFORMATION

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Murat Olutas: Conceptualization, Methodology, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing, Visualization

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Solvatochromic and Solid-State Emissive Azlactone-Based AIEE-Active Organic Dye: Synthesis, Photophysical Properties and Color-Conversion LED Application

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Conflict of Interest:

The authors declare no financial competing financial interest.

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Highlights

- A new donor-acceptor structured Azlactone-based fluorescent dye has been synthesized.
- DFT/TD-DFT calculations and solvatochromic shift methods were carried out.
- ICT character of the dye governs the fluorescence properties in solution.
- Enhanced PL emission was obtained in aggregation- and solid-state than those in solutions.
- The dye was used as a color-conversion material in solid-state lighting application.

Solution