Installation/Modulation of the Emission Response via Click Reaction

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Supporting Information

ABSTRACT: We have demonstrated the installation of a fluorescence property into a nonfluorescent precursor and modulation of an emission response of a pyrene fluorophore via click reaction. The synthesized fluorophores show different solvatochromicity and/or intramolecular charge transfer (ICT) feature as is revealed from the UV-visible, fluorescence photophysical properties of these fluorophores, and DFT/TDDFT calculation. We observed that some of the synthesized fluor-



ophores showed purely ICT character while emission from some of them arose from the LE state. A structureless and solvent polarity-sensitive dual emission behavior was observed for one of the triazolylpyrene fluorophores that contains an electrondonating -NMe2 substituent (fluorophore, 7a). Conversely, triazolylpyrene with an electron-withdrawing -CN group (fluorophore, 7b) showed a solvent polarity-independent vibronic emission. The effect of ICT on the photophysical properties of these fluorophores was studied by fluorescence emission spectra and DFT/TDDFT calculations. Fluorescence lifetimes were also measured in different solvents. All of our findings revealed the delicate interplay of structure and emission properties and thus having broader general utility. As the CT to LE intensity ratio can be employed as a sensing index, the dual emissive fluorophore can be utilized in designing the molecular recognition system too. We envisage that our investigation is of importance for the development of new fluorophores with predetermined photophysical properties that may find a wide range of applications in chemistry, biology, and material sciences.

■ INTRODUCTION

Fluorescent organic molecules have been well-known for a long time for probing biomolecular structure, properties, and functions.¹ However, the photophysical properties of many of the fluorophores sometimes could not be interrelated with their structure due to the deficiency of distinct rationale for their design. Moreover, many of the fluorophores are neither long wavelength emissive nor solvatochromic and hence, disabling their use in cell or in sensing the change in microenvironment in the biological world. Therefore, the design of microenvironment sensitive as well as long wavelength emissive organic fluorophores with a predictable photophysical property in relation to their designed structures via a simple and versatile method is highly desirable for such biochemical applications.1 The excellent regioselectivity, simplicity along with the versatility of the reaction conditions, render "click chemistry" advantageous for synthesizing small organic fluorescent molecules and for achieving the selective coupling of small fluorogenic molecules within a complex biological environment, which enhances greatly the efficiency of biological studies aimed at understanding the natural biological processes via a signal generation.^{1,2}

Only recently, have a few numbers of click fluorescent molecules been reported wherein the intrinsic fluorescence property of the well-explored fluorophores is tuned.^{1c,3} However, the research efforts toward the installation of the fluorescence property into a nonfluorescencet precursor and/or the modulation of the emission response of a weakly fluorescent molecule via "click chemistry" and thereby the synthesis of new solvatochromic click-fluorophores has

been given limited attention. Here, we want to report our design toward the installation of an emission property into a nonfluorescent precursor on one hand and the modulation/enhancement of an emission response of a weakly fluorescent molecule via click chemistry on the other hand (Figure 1). The main importance of our work is that we utilized readily available nonfluorescent starting materials of very low cost and installed an emission property via triazole formation. The synthesized fluorophores are solvofluorochromic and thus can be used for applications in chemistry, material science, and other related areas of interest.^{1e,2b,3}

RESULTS AND DISCUSSION

In our design donor and acceptor units are linked via a triazole moiety so as to allow a charge transfer process that leads to an installation of a fluorescence emission onto a nonfluorescent precursor (Figure 1). We have also focused on the design of a triazolyllinked intrinsic fluorophore for modulation of its emission response. For this purpose we have chosen a versatile fluorophore, pyrene, which shows featured excimer/monomer emission and long fluorescence lifetime. However, the pyrene fluorophore suffers from short emission wavelength, which makes it difficult to use for applications such as in vivo fluorescence imaging. Therefore, preparation of long wavelength emissive and solvatochromic pyrene derivatives is of immense importance.4-6 Thus, we have designed pyrene-based

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Figure 1. (a) Schematic presentation of the fluorescence installation/modulation via click reaction and (b) the chemical structures of the azides and alkynes used in this study.

Scheme 1. (a) General Procedure for the Synthesis of Aromatic Azides and Click Fluorophores and (b) Chemical Structures of the Synthesized Fluorophores

(a) General procedure for the synthesis of aromatic azides and click fluorophores





fluorophores keeping in mind that the electron-donating property of the triazolyl ring may effectively modulate the emission response of an electronically coupled pyrene (Figure 1).

Synthesis. The synthesis was accomplished (Scheme 1) via a modified click reaction protocol² and the products obtained in moderate to high yields were characterized well by NMR, mass, and in some cases single crystal X-ray analysis. Thus, to a 1:1 dichloromethane:ethanol solution of aryl azides (A–D, Figure 1; synthesized via a diazotization reaction of the corresponding aryl amines and subsequent treatment with sodium azide), 1.5 equiv of alkyne (E and F, Figure 1) was added. After 5 min of degassing with N_2 and stirring, a solution of sodium ascorbate (6 mol %) followed by a solution of $CuSO_4$ in water (1 mol %) was added to the reaction mixture. After completion of the reaction monitored by TLC, the reaction mixture was evaporated to dryness, partitioned between water and ethyl acetate. The organic layer was washed with water and brine, then dried over Na2SO4. The final product was obtained in purity by column chromatography and characterized. While compounds 4a, b (Figures 2, 3), 5a, b (see SI, Figure S9, S10), and 6a, b (see SI, Figure S11, and Figure 4, respectively) are designed to show an installation of a fluorescence response into

nonfluorescent precursor amines or alkynes, compounds 7a,b (Figure 5, 6) have been synthesized to show the modulation of an emission response of pyrene (Figure 1 and Scheme 1).

ARTICLE

Studies of Photophysical Properties. Having all the products in hand, we have studied, first, their photophysical properties in different solvents of varying dielectric constants. The aim of this study is to explore the effect of solvent polarity on the fluorophores' photophysical properties and to correlate these effects to their structure.

Whereas solvent polarity has only a minor influence on the absorptive properties of almost all the fluorophores, it drastically affects their emission properties. We have observed that all the products showed an increase in fluorescence intensity over their parent amine or the alkyne precursors. It has also been found that the responses of some of the products are highly sensitive toward a solvent's dielectric constant leading to a red-shifted emission. In general, the fluorophore of the type D(donor)-T(triazole)-A-(acceptor) wherein the precursor amine and alkyne contain a donor -OMe group and an acceptor -CN group, respectively, as in the case of 4b, showed a structureless emission with a red shift (Figure 3b). Also, the quantum yield is increased as the solvent

polarity is increased (Table 1). These results infer an intramolecular charge transfer (ICT) feature of the lowest-lying excited state,⁷ which is supported by a solvatochromicity test (Figure 3c).

 Table 1. Fluorescence Photophysical Properties of the

 Fluorophores^a

			$ au_1$	$ au_2$	$\langle \tau \rangle$	$k_{ m f}$	$k_{ m nr}$
entry	solvents	Φ_f	[ns]	[ns]	[ns]	$[10^8 \text{ s}^{-1}]$	$[10^8 \text{ s}^{-1}]$
4a	dioxane	0.052	0.78	2.71	0.847	0.79	11.01
	DMSO	0.308	0.41		0.41	7.5	17
	EtOH	0.093	7.08		7.08	0.13	1.28
	15% H ₂ O	0.094	8.26		8.26	0.11	1.88
4b	dioxane	0.010	0.04	3.06	0.06	1.63	165.0
	DMSO	0.619	3.06		3.06	2.02	1.24
	MeOH	0.46	1.75		1.75	2.6	3.08
	50% H ₂ O	0.623	3.45		3.45	1.8	1.09
7a	hexane	0.180	0.81	2.50	0.986	1.82	8.31
	toluene	0.202	1.59	3.26	2.463	0.82	3.23
	dioxane	0.076	2.95	6.57	3.256	0.23	2.83
	EtOAc	0.022	3.87		3.87	0.13	2.44
	CHCl ₃	0.059	2.62		2.62	0.40	3.40
	MeOH	0.003	1.87	14.30	8.988	0.003	1.1
	10% H ₂ O	0.019	1.70	5.47	2.285	0.09	4.28
7b	hexane	0.071	1.40	8.71	6.655	0.10	1.39
	DMSO	0.39	16.49		16.49	0.23	0.37
	MeOH	0.13	14.99		14.99	0.08	0.58

^{*a*} Excitation at λ_{ex} nm and recorded at λ_{max} , $\langle \tau \rangle$, k_{f} and k_{nr} are weighted means from the biexponential fits: $\langle \tau \rangle = 1/(\alpha_1/\tau_1 + \alpha_2/\tau_2)$, $k_f = \Phi_f/\langle \tau \rangle$, and $k_{nr} = (1 - \Phi_f)/\langle \tau \rangle$.^{7c,g}

Table 2. The Dipole Moment and Excitation Energy Values of 4a, 4b ,and 7a

$\Delta \mu$ in debye	$4a^a$	$4b^a$	$7a^a$
$\Delta \mu^b = (\mu_{\rm e} - \mu_{\rm g})$	24	21	21
excitation energy (calcd) in eV	4.55	4.14	3.54
excitation energy (exptl) in eV	4.27	4.35	3.61

^{*a*} Onsager radii for **4a**, **4b**, and **7a** are 6.6, 7.2, and 6.3 Å, respectively (obtained from B3LYP/6-31G* optimized geometry). ^{*b*} Calculated from eq 2 and slope from the plots of $\Delta \tilde{\nu}$ values against Δf .

We have observed structureless, broad, and strong solvent polarity dependent dominant emission from the fluorophore **4a** (a **D-T-D** system) (Figure 2b). Thus, **4a** showed a 122 nm redshifted emission when compared between the solvent hexane (almost zero intensity) and MeOH. Upon titration of a dioxane solution of **4a** by water a red shift of 129 nm was observed in 50% water (Figure 2c). These features indicate an emission from an ICT state.^{7,8} Fluorescence quantum yields are also found to be increased with the increase in solvent polarity (Table 1). This clearly indicates a highly polar emissive state. However, it is decreased in MeOH and ethanol, which may be due to a protic solvent—solute interaction.^{7a,9}

Fluorophore **6b** showed a comparatively less solvent polarity sensitive emission that is centered at around 406 nm. A spectral shift of only 23 nm is observed with a decrease in intensity as we move from hexane to MeOH. This result is clearly an indication of an ICT emission (Figure 4).

Compounds 5a,b and 6a showed only faint emission under the condition used for others. However, at large slit width, the following behaviors were observed where quantum yields could not be calculated. Thus, fluorophore **5b** (A-T-A system) showed a solvent polarity independent structured emission (see SI, Figure S10). A highly solvent polarity dependent emission was exhibited by fluorophore 5a, an A-T-D system. Thus, as the solvent polarity increased, a shift of 56 nm from cyclohexane to MeOH with decreased intensity was observed, which is characteristic of ICT emission (see the SI, Figure S9). Fluorophore 6a exhibited a dual behavior similar to that of 7a in low polar solvents, but a single emission centered at 357 nm appeared in high polar solvents like ACN, DMSO, and MeOH. In low polar solvents like hexane, cyclohexane, ether, 1,4-dioxane, toluene, chloroform, and ethyl acetate, the second band at 399 nm in hexane shifted gradually with a decrease in intensity as the polarity increases and reaches 537 nm in ethyl acetate, which again inferred an emission from ICT state (see the SI, Figure S11).

We have observed an interesting fluorescence photophysical property exhibited by the fluorophore 7a (an A-T-D system), a triazolyl modified pyrene. Thus, the fluorophore 7a showed a strong structureless emission centered at 415 nm in hexane and cyclohexane. However, in ether, dioxane, toluene, CHCl₃, and EtOAc, a dual emission behavior has been observed with a strong red-shifted pattern of the ICT band as the solvent polarity is increased from toluene (466 nm) to EtOAc (544 nm) (Figure 5b).



Figure 2. UV–visible (a) and fluorescence spectra (b) of **4a** in different solvents and fluorescence in dioxane–water solvent system (c) (10 μ M, rt; $\lambda_{ex} = \lambda_{max}$ of each solvent).



Figure 3. UV–visible (a) and fluorescence spectra (b) of 4b in different solvents and fluorescence in dioxane–water solvent system (c) (10 μ M, rt; $\lambda_{ex} = \lambda_{max}$ of each solvent).



Figure 4. UV-visible (a) and fluorescence spectra (b) of 6b in different solvents (10 μ M, rt; $\lambda_{ex} = \lambda_{max}$ of each solvent).

In highly polar solvents like ACN and MeOH, a structured band characteristic of a pyrene emission with a very low intensity has been observed that is also supported by a solvatochromicity test (Figure 5c). Thus, in pure dioxane, the ICT emission is highly dominated over the LE emission and as the percent of H₂O is increased, the intensity of the LE emission is also going to increase. However, in 50% H₂O in dioxane, we have observed a pure LE emission (Figure 5c). Compared to pyrene-amine, 7a showed about 100 nm of red-shifted emission in polar solvents. On the other hand, in the case of the fluorophore 7b (D-T-A system), which contains an electron-withdrawing -CN substituent, the emission is centered at 400 nm, and the vibronic structure of a pyrene emission is maintained, i.e., the emission originates from a purely LE state (Figure 6b).^{7c,10} The fluorescence quantum yield of 7b is increased as the solvent polarity is increased with no solvatochromicity (see the SI, Table S5) while it is lower in a polar solvent than that in a nonpolar solvent in the case of 7a (Table 1, and see Table S5 in the SI). These results infer an ICT feature of the lowest-lying excited state in 7a (with the pyrene as an electron acceptor) but not in 7b.7,8,10

Therefore, our study clearly shows that a "click" reaction between an azide and an alkyne sufficiently installs a fluorescence emission property into a nonfluorescent precursor and modulates the emission response of a pyrene fluorophore. It is important to note that these fluorophores show a direct trend between the fluorescence intensities and solvent dielectric constants and thus have a broader general utility (see the SI, Figures S5–12). Examination of the band-shape and fluorescence quantum yields of the fluorophores reveals the delicate interplay of structure and emissive states. Thus, compounds **4a**, **4b**, and **6b** showed a highly emissive, pure ICT state as is indicated by a high quantum yield, broad band-shape, and red-shifted pattern as the solvent polarity is increased. The solvent polarity independent LE emission of **7b** suggests the emitting state as a nonpolar ${}^{1}\pi - \pi^{*}$ state. The dual emission exhibited by **7a** indicates the presence of a mixed LE and CT state. Switching between these two states depends on the structure and the solvent polarity.^{8,10e}

To get an insight into the different solvatochromic behaviors of **4a**,**b** and **7a**,**b**, the spectral dependency on solvent polarity was studied on the basis of the Lipert–Mataga model.¹¹ The Lippert–Mataga polarity parameter (Δf) has been considered as the measure of the polarity of different solvents and solvent mixtures used and was calculated by using the following eq 1.^{11–14}

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{1}$$

Thus, the absorption (λ_{\max}^{abs}) and fluorescence (λ_{\max}^{fl}) maxima of the more intense fluorophores **4a**,**b** and **7a** were measured in different solvents and solvent mixtures along with the polarity



Figure 5. UV-visible (a) and fluorescence spectra (b) of 7a in different solvents and fluorescence in dioxane-water solvent system (c) (10 µM, rt; $\lambda_{ex} = \lambda_{max}$ of each solvent) showing a dual behavior.



Figure 6. UV-visible (a) and fluorescence spectra (b) of 7b in different solvents (10 μ M, rt; $\lambda_{ex} = \lambda_{max}$ of each solvent).

parameter Δf of the different solvent systems calculated with eq 1 (see the SI, Table S3). As is revealed from the UV-visible and fluorescence spectra (Figures 2 and 3 for 4a,b and Figures 5 and 6 for 7a,b, respectively), the λ_{\max}^{fl} values gradually undergo a red shift when the solvent polarity increases for all the florophores. However, the red shift of λ_{max}^{fl} is much larger than the shift in λ_{max}^{abs} values, suggesting the fluorescent states of all the fluorophores to be more polar in nature than their ground states.^{7c,10g,11b,11c,14b,15-17} In particular, fluorophore **4a**,**b** showed a slight red shift with Δf in the lower solvent polarity region ($\Delta f < 0.265$) but at the higher solvent polarity region the λ_{\max}^{abs} values showed a small blue shift (see the SI, Table S3). However, as the solutions of 4a,b in dioxane were titrated with water, a normal red shift was observed for 4a while a blue shift was the result for fluorophore 4b. The $\lambda_{\max}^{\rm fl}$ values gradually undergo a more red shift when the solvent polarity increases for 4a,b. In the case of fluorophore 7a, the λ_{max}^{abs} values showed a very small red shift in low polar solvents and a blue shift in high polar solvents; however, in the dioxane-water solvent system the λ_{\max}^{abs} remains almost unchanged. A similar behavior was observed for fluorophore 7b. However, the $\lambda_{\text{max}}^{\text{fl}}$ of the ICT band shifted much more to the red for 7a while an unchanged but increased intensity of the λ_{max}^{II} was observed for 7b as the solvent polarity is increased.

Next, we examined the correlations of the absorption and fluorescence maxima ($\tilde{\nu}_{max}^{abs}$ and $\tilde{\nu}_{max}^{fl}$ respectively, in cm⁻¹) of the fluorophore 4a,b and 7a, respectively, with the solvent polarity function Δf (Figure 7a-c). Thus, from Figure 7b and c it is seen that for the fluorophore 4b, and 7a, the $\tilde{\nu}_{abs}$ values apparently correlate linearly with Δf , suggesting that the ground state of these fluorophores is moderately polar in nature. For the fluorophore 4a, a smaller correlation is observed for the $\tilde{\nu}_{abs}$ vs Δf plot (Figure 7a). However, following the UV-visible spectra (Figurea 2a and 3a for 4a and 4b, respectively), which is quite similar to that of the 4b, we expect that the ground state of the 4a is also of polarity similar to that of the 4b.

However, as is shown in Figure 7a–c, the $\tilde{\nu}_{\rm fl}$ values for all the fluorophores show a very good linear correlation with Δf for the whole range of the solvent polarity tested. This observation, therefore, suggests that for all the fluorophores the nature of the fluorescent states remains essentially unchanged in all the solvents used. However, the spectral feature changes significantly due to the solvent-induced modulation. The reasonably high slopes of the $\tilde{\nu}_{\rm fl}$ vs Δf plots for all the fluorophores further suggest that the fluorescent states of these fluorophores are highly polar in nature, most possibly of intramolecular charge transfer (ICT) character.^{7,8,10,15-1}

In different solvents, the absorption and fluorescence spectra involve the electronic transitions between the same two ground and excited electronic states, and the Stokes' shift $(\Delta \tilde{\nu})$ is expected to follow a linear relation with Δf_{t} , as suggested by the Lippert and



Figure 7. Plots of $\tilde{\nu}_{fl}$ and $\tilde{\nu}_{abs}$ values against Δf for fluorophore 4a (a), 4b (b), and 7a (c) ($\tilde{\nu}_{fl(ICT)}$ and $\tilde{\nu}_{abs}$ values) in different solvents.



Figure 8. (a) A plot of $\Delta \tilde{\nu}$ vs Δf of **4a**, **4b**, and **7a**, and (b) proposed photophysical process for the dual emission.

Mataga eq 2^{12–14}

$$\Delta \tilde{\nu} = \Delta \tilde{\nu}_0 + \frac{2(\mu_e - \mu_g)^2}{hcr^2} \Delta f$$
(2)

where μ_{e} and μ_{g} are the excited (fluorescent) state and the ground state dipole moments of the fluorophore, h is Planck's constant, c is the velocity of light, and *r* is the Onsager radius of the dipole–solvent interaction sphere. The $\Delta \tilde{\nu}$ values for 4a, 4b, and 7a (for the long wavelength emissive band) in different solvents were calculated (in cm⁻¹) (see the SI, Table S2) and the $\Delta \tilde{\nu}$ was ploted against the solvent polarity Δf following eq 2. Thus, it is seen from the plot that the $\Delta \tilde{\nu}$ (Figure 8a) values correlate linearly well with the Δf values for all the solvents studied. Linear correlation with large slopes of the $\Delta \tilde{\nu}$ vs Δf plots suggests that the fluorescence states are highly polar in nature for all the fluorophores. Considering the Onsager radius r values for the fluorophores given in the footnote of Table 2 (obtained from geometry optimized structures at the B3LYP/6-31G* level¹⁸), the $(\mu_e - \mu_g)$ values for 4a,b and 7a are estimated by using the slopes of the respective $\Delta \tilde{\nu}$ vs Δf plots and are found to be about 24.0, 21.0, and 21.0 D, respectively. Substantially high values of $(\mu_e - \mu_g)$ thus obtained from the plot (Figure 8a and Table 2) suggest that the fluorescence states of all these fluorophores are of strong ICT character, which was inferred earlier. The $(\mu_{\rm e} - \mu_{\rm g})$ value for 4a is somewhat higher than that of the 4b and 7a, which indicates a higher ICT character of 4a compared to others. Comparing the spectral behaviors and all the experimental results, it is clear that the ICT state is developed from the LE state in the case of 7a (Figure 8b).

Theoretical Calculation. To investigate the relation between the polarity-dependent emission and the ICT feature, we have carried out TDDFT calculations using the Gaussian 03 program package¹⁸ (see the SI, Figures S16–23 and Table S6). Thus, as revealed from the overlapping of HOMO–LUMO as well as the transition oscillator strength, the electronic transitions of $S_0 \rightarrow S_1$ are fully allowed for all the fluorophores (Figure 9, and in the SI Figures S16-23, and Table S6). This means that reverse transition, i.e., $S_0 \leftarrow S_1$, is also fully allowed indicating the potential fluorophoric nature of the molecules. The emissive state of 7b and 5b is basically a locally excited (LE) state as is suggested by the HOMO–LUMO distributions. For 4b (Figure 9b), 5a, and 6b, however, the emissive state is characterized with more significant electron redistribution, i.e., ICT feature. Calculated results supported our above explanation.¹⁹ Calculated excitation energies for the transition of $S_0 \rightarrow S_1$ of 7b and 5b are 355 and 358 nm (in vacuum), respectively. These values are close to the experimental result of 342 and 278 nm (in hexane), respectively. The excitation energies for the same transition of 4b, 5a, and 6b are 299, 547, and 318 nm (in vacuum), respectively. These values are close to the experimental result of 293 (in toluene), 290 (in dioxane), and 300 nm (in dioxane), respectively. These calculations rationalized the explanation of ICT origin of the solvent polarity dependency of the fluorophores' emission (Figures S17, S18, and S21, respectively, in the SI). Fluorophore 7a and 6a showed dual emission, which again depends on solvent polarity, thus showing an emission from both LE and CT states. The excitation energies for the transition of $S_0 \rightarrow S_1$ of 4a, 7a, and 6a are 330, 447, and 419, respectively, which are closer to the experimental results (experimental: 294, 340, and 292 nm in hexane, respectively). Fluorophore 4a showed a strong ICT emission (Figure 9a) and 7a showed dual emission, which again depends on solvent polarity, thus showing an emission from both LE and CT states. For fluorophore 7a, the $S_0 \rightarrow S_1$ transition is excited at a much longer wavelength of 447 nm (exptl in hexane 340 nm) with an *f* value of 0.10. The transition $S_0 \rightarrow S_2$ (349 nm, in vacuum) is, however, closer to the experimental value with higher f value (f = 0.39) indicating that the S₂ state is populated well (Figure 9c and in the SI, Figure S22).

As revealed from the overlapping of HOMO–LUMO as well as the transition oscillator strength for all the fluorophores except for **6a** all the electronic transitions of $S_0 \rightarrow S_1$ are allowed. This means that reverse transition, i.e., $S_0 \rightarrow S_1$, is also fully allowed indicating the potential fluorophoric nature of the molecules. For molecule **6a**, however, the $S_0 \rightarrow S_1$ transition is excited at a much longer wavelength of 419 nm with an *f* value of 0.0651 (see the SI, Figure S20). This small *f* value indicated the very weakly fluorescent properties of **6a**, which was true as we did not see any fluorescence for it under the same condition as for the other fluorophores. For **5a**, however, the $S_0 \rightarrow S_1$ transition is excited at a much longer wavelength of 547 nm (2.27 eV, expt1 in dioxane 290 nm) with an *f* value of 0.119 (see the SI, Figure S18).

The emissive state of 7b is basically a locally excited (LE) state as is suggested by the HOMO–LUMO distributions. For 4band 6b, however, the emissive state is characterized with more



Figure 9. HOMO and LUMO of the representative fluorophores (a) 4a, (b) 4b, and (c) 7a.

Table 3.	Fluorescence	Lifetime	Dependence	on	Wavelength of 7a
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entry	solvents	$\Phi_{ m f}$	λ [nm]	$ au_1 [m ns]$	$\tau_2 [ns]$	$\langle \tau \rangle [\rm ns]$	$k_{\rm f} [10^8 { m s}^{-1}]$	$k_{\rm nr} [10^8 {\rm s}^{-1}]$
7a	dioxane	0.001	406	3.78 (29.0%)	2.00 (71.0%)	2.317	0.33	3.98
		0.076	496	2.95 (82.7%)	6.57 (17.3%)	3.256	0.23	2.83
	EtOAc	0.030	385	3.27 (5.9%)	1.27 (94.1%)	1.305	0.39	7.26
		0.022	548	3.87 (100%)		3.87	0.13	2.44
	CHCl ₃	0.058	384	7.20 (100%)		7.20	0.14	1.24
		0.059	498	2.62 (100%)		2.62	0.40	3.40
	10% H_2O in dioxane	0.003	401	4.27 (11.7%)	2.56 (88.3%)	2.685	0.08	3.64
		0.019	577	1.70 (63.0%)	5.47 (37.0%)	2.285	0.09	4.28

significant electron redistribution, i.e., ICT feature. Calculated results support our above explanation (see the SI, Table S6).¹⁹ Fluorophore **4a** showed a strong ICT emission and **7a** showed a dual emission, which again depends on solvent polarity. Therefore, an emission from both the LE and ICT states has been observed in the case of **7a** (see the SI, Table S6).

Fluorescence Lifetime Measurement. To interpret the photophysical properties in a more intuitive manner, the fluorescence lifetimes of 4a,b, 6b, and 7a,b were measured in different solvents. Thus, biexponential decay is observed in nonpolar dioxane or hexane and the lifetimes of the major components are less than or closer to 1.0 ns (Table 1). However, as the solvent polarity is increased, lifetimes are also increased. As for example, in dioxane, the major component (68%) of fluorophore 4b is short-lived ($\tau_1 = 0.04 \text{ ns}$) and its relative contribution is increased to 100% in 1:1 dioxane:water solution (τ_1 = 3.45 ns), which is an indication of a ${}^{1}\pi - \pi^{*}$ state. In protic polar solvent, like methanol, compared to DMSO, the lifetime of 4b is decreased, which may be because of the fluorescence quenching through the nonradiative pathway via hydrogen bonding.^{7a} The relative contribution of the longer lifetime component of 7a ($\tau_2 = 2.5$ ns) in hexane is increased from 27% to 100% as the solvent polarity is increased (in CHCl₃, τ_1 = 2.62 ns). In methanol, the minor component showed a decay time τ_1 of 1.87 ns, for which a weak emission from LE state was observed. No ICT emission has been observed as the decay time of the major component ($\tau_1 = 14.30$ ns) is very large and the fluorophore followed a nonradiative pathway.

Lifetime data were also collected at two emission maxima for 7a in solvents displaying biexponential decays (Table 3). Thus, it has been observed that the values of τ_1 and τ_2 remain consistent, but the relative contributions of the two lifetimes vary according to the observed wavelength. As for example, for 7a, in dioxane, the relative contribution of the longer lifetime τ_1 is increased from 29% to 83% as the observed wavelength is increased from 406 to 496 nm. Similar behavior was observed in 10% water in dioxane solvent. As the intensity of the LE band is increased from dioxane to 10% water in dioxane solution, the lifetime is also increased

from 3.78 to 4.27 ns (monitoring wavelength is the LE band). This observation correlates with the $k_{\rm nr}$ value that is decreased from 3.98 to 3.64 ns. When the monitoring emission wavelength is the ICT band, we have observed that with decrease in intensity, the lifetime is also decreased from 2.95 ns to 1.70 ns, which again correlates with the increased $k_{\rm nr}$ value of 4.28 ns from 2.83 ns.

In conclusion, we have been able to install the fluorescence response into a nonfluorescent precursor and modulate the emission response of a pyrene fluorophore via click reaction. Our findings reveal the delicate interplay of structure and emission properties, thus having a broader general utility. As the ICT to LE intensity ratio can be employed as a sensing index, the dual emissive fluorophore can be utilized in designing molecular recognition systems. Our investigation on the photophysical properties of click chemistry derived fluorophores is of immense importance for the development of new fluorophores with predetermined photophysical properties that may find a wide range of applications in chemistry, biology, or material sciences. Currently, the exploration of the dual fluorescent probe as a metal ion sensor is under investigation.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under a nitrogen atmosphere in flame-dried glassware, using a nitrogen filled balloon. Organic extracts were dried over anhydrous sodium sulfate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (60–120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F254 (0.25 mm). ¹H NMR spectra were recorded at 400 MHz and ¹³C NMR spectra were recorded at 100 MHz. Coupling constants (*J* value) were reported in hertz. The chemical shifts were shown in ppm downfield from tetramethylsilane, using residual chloroform ($\delta = 7.24$ in ¹H NMR, $\delta = 77.23$ in ¹³C NMR), dimethyl sulfoxide ($\delta = 2.48$ in ¹H NMR, $\delta = 39.5$ in ¹³C NMR), as an internal standard. Mass spectra were recorded with an HR mass spectrometer and data analyzed by using the built-in software. IR spectra were recorded in KBr or neat on a FT-IR spectrometer.

General Procedure for the Preparation of Aryl Azides. An ice cold solution of sodium nitrite (3 equiv) in water was added dropwise

to a cold solution of aryl amine 1 (1 equiv) in water and concentrated hydrochloric acid at 0 °C over 7–10 min. The reaction mixture was slowly stirred for 1–2 min before an ice cold solution of sodium azide (6 equiv) in water was added dropwise at 0 °C over 10 min. The mixture was stirred for 15 min. The resulting mixture was extracted with ether. The organic layer was washed with water, followed by a brine solution, dried over anhydrous Na₂SO₄, and then concentrated to yield pure aryl azides 2 (average yield 60–90%). Formation of the product azide was confirmed from IR study (1-azido-4-methoxybenzene (A): yield 60%; IR: 2105 cm⁻¹; 1-azido-4-nitrobenzene (B): yield 62%; IR 2126 cm⁻¹; 1-azido-yrene (D): yield 75%; IR 2133 cm⁻¹) and the produced azides were then immediately used for the next step without further purification.

General Procedure for the [3 + 2] Cycloaddition of Azides and Terminal Alkynes. In a round-bottomed flask fitted with a septum, azide 2 (1.0 equiv) was dissolved by dry 1:1 dichloromethane and ethanol and degassed for 5 min with N₂. Then, alkyne 3 (1.5 equiv) was added and both the stirring and degassing were continued for the next 5 min. After that a 6 mol % sodium ascorbate was added. The reaction mixture was stirred for 5 min before 1 mol % powdered CuSO₄ was added. Degassing was continued for the next 10 min. The reaction was allowed to proceed to room temperature and monitored by TLC. After total consumption of the starting azide, the reaction mixture was evaporated completely to a solid material and partitioned between water and ethyl acetate. The organic layer was washed with water followed by brine solution, dried over Na₂SO₄, and then concentrated. The title triazolyl compounds were separated by column chromatography and characterized. The average yields were 50% to 85%.

Synthesis of 4-(1-(4-Methoxyphenyl)-1*H*-1,2,3-triazol-4yl)-*N*,*N*-dimethylbenzenamine (4a). Using the general procedure, starting from 0.116 g of 1-azido-4-methoxybenzene A and 0.169 g of E, 0.137 g of the title compound 4a was isolated as a white solid (60%). IR (KBr) 1618, 1593, 1518, 1503, 1354, 1250, 1040, 808 cm⁻¹; ¹H NMR (CDCl₃; 400 MHz) δ 3.01 (6H, s), 3.87 (3H, s), 6.81 (2H, d, *J* = 7.2 Hz), 7.03 (2H, d, *J* = 7.6 Hz), 7.68 (2H, d, *J* = 8.0 Hz), 7.77 (2H, d, *J* = 8.0 Hz), 7.98 (1H, s); ¹³C NMR (CDCl₃; 100 MHz) δ 40.7, 55.8, 112.8, 114.9, 116.5, 118.9, 122.2, 126.9, 130.9, 148.9, 150.6, 159.8; HRMS calcd for C₁₇H₁₈N₄O ([M + H]⁺) 295.1559, found 295.1562.

Synthesis of 4-(1-(4-Methoxyphenyl)-1*H*-1,2,3-triazol-4yl)benzonitrile (4b). Using the general procedure, starting from 0.116 g of 1-azido-4-methoxybenzene A and 0.148 g of F, 0.144 g of the title compound 4b was isolated as a white solid (67% yield). IR (KBr) 2231, 1611, 1519, 1489, 1258, 1025, 825 cm⁻¹; ¹H NMR (CDCl₃; 400 MHz) δ 3.87 (3H, s), 7.04 (2H, d, *J* = 8.8 Hz), 7.66 (2H, d, *J* = 8.8 Hz), 7.73 (2H, d, *J* = 8.0 Hz), 8.00 (2H, d, *J* = 8.0 Hz), 8.18 (1H, s); ¹³C NMR (CDCl₃; 100 MHz) δ 55.8, 111.8, 115.1, 118.9, 119.2, 122.4, 126.3, 130.3, 132.9, 134.9, 146.5, 160.3; HRMS calcd for C₁₆H₁₂N₄O ([M + H]⁺) 277.1089, found 277.1091.

Synthesis of *N*,*N*-Dimethyl-4-(1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl)benzenamine (5a). Using the general procedure, starting from 0.067 g of 1-azido-4-nitrobenzene B and 0.090 g of E, 0.050 g of the title compound 5a was isolated as a orange solid (50%). IR (KBr) 1621, 1595, 1517, 1497, 1368, 1335, 853 cm⁻¹; ¹H NMR (CDCl₃; 400 MHz) δ 3.00 (6H, s), 6.78 (2H, d, *J* = 6.8 Hz), 7.08 (2H, d, *J* = 8.8 Hz), 7.59 (2H, d, *J* = 8.8 Hz), 7.77 (1H, s), 8.28 (2H, d, *J* = 8.8 Hz); ¹³C NMR (CDCl₃; 100 MHz) δ 41.1, 113.5, 125.0, 125.5, 126.2, 129.9, 131.1, 133.6, 138.5, 141.9, 147.6; HRMS calcd for C₁₆H₁₅N₅O₂ ([M + H]⁺) 310.1304, found 310.1309.

Synthesis of 4-(1-(4-Nitrophenyl)-1*H*-1,2,3-triazol-4-yl)benzonitrile (5b). Using the general procedure, starting from 0.064 g of 1-azido-4-nitrobenzene **B** and 0.075 g of **F**, 0.017 g of the title compound **Sb** was isolated as a yellow solid (51%). IR (KBr) 2228, 1612, 1594, 1521, 1490, 1366, 1338, 854 cm⁻¹; ¹H NMR (CDCl₃; 400 MHz) δ 7.35 (2H, d, *J* = 8.4 Hz), 7.54 (2H, d, *J* = 8.8 Hz), 7.70 (2H, d, *J* = 8.0 Hz), 7.95 (1H, s), 8.33 (2H, d, *J* = 8.8 Hz); ¹³C NMR (CDCl₃ + d_6 -DMSO; 100 MHz) δ 113.2, 117.4, 124.8, 125.3, 129.0, 130.1, 132.6, 134.4, 136.0, 140.3, 147.5; HRMS calcd for C₁₅H₉N₅O₂ ([M + H]⁺) 292.0834, found 292.0840.

Synthesis of 4-(1-(5-Bromonaphthalen-1-yl)-1*H*-1,2,3-triazol-4-yl)-*N*,*N*-dimethylbenzenamine (6a). Using the general procedure, starting from 0.045 g of 1-azido-5-bromonaphthalene C and 0.040 g of E, 0.060 g of the title compound 6a was isolated as a pink solid (85%). IR (KBr) 1617, 1597, 1498, 1352, 802, 780, 532 cm⁻¹; ¹H NMR (CDCl₃; 400 MHz) δ 2.99 (6H, s), 6.79 (2H, d, *J* = 8.8 Hz), 7.34 (1H, t, *J* = 8.0 Hz), 7.67 (3H, m), 7.79 (2H, d, *J* = 9.2 Hz), 7.86 (2H, d, *J* = 6.8 Hz), 7.98 (1H, s), 8.44 (1H, dd, *J* = 1.4, 7.6 Hz); ¹³C NMR (CDCl₃; 100 MHz) δ 40.6, 112.7, 118.2, 121.1, 122.8, 123.3, 124.6, 126.5, 127.0, 128.2, 129.7, 130.2, 131.4, 132.9, 134.4, 148.6, 150.8; HRMS calcd for C₂₀H₁₇N₄Br ([M + H]⁺) 393.0715, found 393.0717.

Synthesis of 4-(1-(5-Bromonaphthalen-1-yl)-1*H*-1,2,3-triazol-4-yl)benzonitrile (6b). Using the general procedure, starting from 0.024 g of 1-azido-5-bromonaphthalene C and 0.018 g of F, 0.02 g of the title compound 6b was isolated as a reddish pink solid (56%). IR (KBr) 2227, 1602, 1591, 1497, 839, 773, 555 cm⁻¹; ¹H NMR (CDCl₃; 400 MHz) δ 7.38 (1H, t, *J* = 8.0 Hz), 7.57 (1H, d, *J* = 8.8 Hz), 7.68 (1H, t, *J* = 6.6 Hz), 7.72 (1H, s), 7.76 (1H, d, *J* = 8 Hz), 7.89 (1H, d, *J* = 7.6 Hz), 8.05 (2H, d, *J* = 8.4 Hz), 8.21 (1H, s), 8.50 (1H, d, *J* = 8.4 Hz); ¹³C NMR (CDCl₃; 100 MHz) δ 112.2, 118.9, 122.4, 123.7, 124.8, 126.5, 128.5, 130.1, 130.4, 131.7, 133.1, 134.7, 146.3; HRMS calcd for C₁₉H₁₁N₄Br ([M + H]⁺) 375.0245, found 375.0248.

Synthesis of *N*,*N*-Dimethyl-4-(1-(pyren-1-yl)-1*H*-1,2,3-triazol-4-yl)benzenamine (7a). Using the general procedure, starting from 0.025 g of 1-azidopyrene (**D**) and 0.022 g of **E**, 0.024 g of the title compound 7a was isolated as a light pink solid (68% yield). IR (KBr) 1617, 1567, 1503, 1460, 1351, 819 cm⁻¹; ¹H NMR (CDCl₃; 400 MHz) δ 3.03 (6H, s), 6.84 (2H, d, *J* = 8.0 Hz), 7.87 (2H, d, *J* = 8.4 Hz), 7.97 (1H, d, *J* = 9.2 Hz), 8.06–8.20 (6H, m), 8.24–8.29 (3H, m); ¹³C NMR (CDCl₃; 100 MHz) δ 40.6, 112.7, 118.6, 121.4, 123.5, 124.3, 124.9, 125.2, 126.1, 126.5, 126.9, 127.1, 128.9, 129.7, 130.8, 131.3, 132.3, 148.6, 150.8; HRMS calcd for C₂₆H₂₀N₄ ([M + H]⁺) 389.1766, found 389.1768.

Synthesis of 4-(1-(Pyren-1-yl)-1H-1,2,3-triazol-4-yl)benzonitrile (7b). Using the general procedure, starting from 0.010 g of 1-azidopyrene (**D**) and 0.008 g of **F**, 0.010 g of the title compound 7**b** was isolated as a brown solid (66% yield). IR (KBr) 2225, 1614, 1489, 1461, 845 cm⁻¹; ¹H NMR (CDCl₃; 400 MHz) δ 7.77 (2H, d, *J* = 7.6 Hz), 7.88 (1H, d, *J* = 8.4 Hz), 8.08–8.29 (10H, m), 8.33 (1H, s); ¹³C NMR (CDCl₃; 100 MHz) δ 112.0, 118.9, 121.0, 123.5, 124.0, 124.3, 124.9, 125.3, 126.5, 126.9, 127.1, 129.4, 130.2, 130.8, 131.3, 132.7, 133.1, 134.9, 146.3; HRMS calcd for C₂₅H₁₄N₄ ([M + H]⁺) 371.1297, found 371.1302.

UV–**Visible Measurements.** All the UV–visible spectra of the compounds (10 μ M) were measured in different solvents, using a UV–visible spectrophotometer with a cell of 1 cm path length.

Fluorescence Experiments. All the sample solutions were prepared as described in UV measurement experiments. Fluorescence spectra were obtained with use of a fluorescence spectrophotometer (for 4a, 4b, and 7a) at 25 °C using a 1 cm path length cell. The fluorescence quantum yields (Φ_f) were determined with quinine sulfate as a reference with the known Φ_f (0.55) in 0.1 M solution in sulfuric acid.

Fluorescence Lifetime Measurements. Fluorescence lifetimes were measured with the use of a system that employs a microchannel plate photomultiplier as the detector. Edinburgh 290 nm (for 4b) and 308 nm Pulsed LED (for 4a) and 375 nm (for 6b, 7a, 7b) Laser Diode were used for excitation. The fluorescence decay was analyzed by reconvolution (for 4a,b) and tail fitting (for 6b, 7a, 7b) method, using built-in software. All experiments were performed at 298 K.

Theoretical Calculation. The ground state structures of the fluorophores were optimized by using density functional theory $(DFT)^{18}$ with B3LYP functional and 6-31G (d) basis set. The excited state related

calculations were carried out with the time dependent density functional theory (TD-DFT) with the optimized structure of the ground state (B3L YP/6-31G(d)). There are no imaginary frequencies in frequency analysis of all the calculated structures, therefore each calculated structure is a local energy minimum.

ASSOCIATED CONTENT

Supporting Information. Full chemical structures, crystallographic data, photophysical spectra and lifetime measurement, Cartesian coordinates, TDDFT calculation, and ¹H /¹³C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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