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Novel Rhodafluors: Synthesis, Photophysical, pH and TD-DFT Studies

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Abstract An efficient protocol for the synthesis of new rhodol derivatives has been developed. The synthesis involves condensation of 2-hydroxy benzophenone derivatives with 1, 3-dihydroxy benzene derivatives in solvents such as ionic liquid (N-methyl-2-pyrrolidonium hydrogen sulfate) and methane sulphonic acid. Both ionic liquid and methane sulphonic acid were found to be promising self-catalyzed solvents to bring out the conversion to form desired rhodols in excellent yields. In N-methyl-2-pyrrolidonium hydrogen sulfate reaction proceeds faster compared to methane sulphonic acid. The new fluorophores are investigated for their photophysical properties in various microenvironments and systematically characterized by means of density functional theory and time dependent density functional theory. Photophysical properties of the new rhodafluors found sensitive towards change in the pH of media and thus can be used as efficient pH sensors.

Keywords DFT \cdot ([HNMP]⁺[HSO₄]⁻) \cdot Methane sulphonic acid \cdot pH study \cdot Rhodafluors \cdot Td-DFT

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Introduction

Rhodol fluorophores are the hybrid structure of fluorescein and rhodamine, and therefore are also named as "Rhodafluor" [1] (Fig. 1). They inherit all the excellent photophysical properties of parents such as high extinction coefficients, quantum yields, photostability, and solubility in a variety of solvents [2]. Moreover the photophysical properties of rhodol fluorophores can be fine-tuned through different substitution patterns on the nitrogen atom [3] and therefore they are subject of interest as fluorescent probes [4].

The synthesis of rhodol derivatives can be achieved by various conventional methods such as condensation using acid catalysts [2, 5], palladium-catalyzed amination reaction [6], Buchwald-Hartwig coupling reaction [7], etc.

Despite their excellent photophysical properties there are only few examples about the applications of rhodol fluorophores [1, 2, 5, 8–11], probably due to the lack of a convenient synthetic methods. Here, we report a highly efficient and environment friendly protocols, mediated by ionic liquid (IL) and methane sulphonic acid (MSA). Ionic liquids are considered as ideal alternatives to volatile organic solvents and widely regarded as environment friendly alternatives to many commonly used solvents [12]. They are good solvents for wide range of both inorganic and organic reactions [13]. Ionic liquids are non-volatile, hence they may be used in highvacuum systems and eliminate many containment problems.

The synthesized rhodofluors are investigated for their photophysical properties in various microenvironments experimentally and systematically characterized by means of DFT and TD-DFT. The photophysical

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Fig. 1 General structures of the Rhodol, Rhodamine and Fluorescein dyes



x[⊖]



properties of the new rhodofluors owing to formation of two different forms are found to be sensitive towards change in pH of phosphate buffer.

Experimental

Reagents and Apparatus

All the chemicals and spectroscopic grade solvents were obtained from the local suppliers like S. D. Fine chemicals and SPECTROCHEM PVT. LTD., unless otherwise mentioned, and used as such without further purifications. All the common chemicals used were of analytical grade. All the reactions were monitored by TLC (thin-layer chromatography) with detection by UV light. ¹H NMR and ¹³C NMR spectra were recorded on Varian 500 MHz instrument using TMS as an internal standard. LCMS spectra were recorded on Finnegan mass spectrometer.

Photophysical Studies

The photophysical studies such as absorption spectra, emission spectra, molar extinction coefficients and quantum yields of fluorescence are determined using dye solutions of 4–10 μ M concentrations. The absorption spectra were recorded at room temperature on the Perkin-Elmer UV-VIS spectrometer, Lambda 25. The emission spectra were recorded at room temperature on VARIAN CARY Eclipse fluorescence spectrophotometer using 10 mm cuvette with 2.5 nm to 5 nm slit width. The comparative quantum yields of fluorescence were calculated by using Rhodamine B in methanol (quantum yield = 0.7) as reference [14] using following Eq. 1.

$$\phi_X = \phi_{ST} \left(\frac{Grad_X}{Grad_{ST}} \right) \left(\frac{\eta_X^2}{\eta_{ST}^2} \right) \tag{1}$$

Where, $_X$ and $_{ST}$ are quantum yield of fluorescence of the sample and reference respectively, $Grad_X$ and $Grad_{ST}$ are slope of the plots of absorbance vs area under curve of corresponding emission spectra of sample and standard respectively, η_X^2 is refractive index of solvent in which quantum yield of sample is being calculated and η_{ST}^2 is refractive index of solvent in which quantum yield of standard is taken as reference.

Oscillator strength (f) was obtained from integrated absorption coefficient of the absorption band by using the Eq. 2,

$$f = 4.32 \times 10^{-9} \int \varepsilon(\vartheta) d\nu \tag{2}$$

The transition dipole moment (μ_{eg}) is related to oscillator strength (f) and calculated from Eq. 3 [15],

$$\mu_{eg} = \sqrt{\frac{3e^2h}{8\pi^2mc}} \times \frac{f}{\vartheta_{eg}}$$
(3)

Where, *m*, $\overline{\vartheta}_{eg}$ and *e* are the mass of electron, absorption frequency, and charge on electron, respectively.

Preparation of Ionic Liquid, N-Methyl-2-Pyrrolidonium Hydrogen Sulphate (1)

The ionic liquid was prepared by following reported protocol [16] in quantitative yields (Scheme 1).

General Procedure for the Preparation of 2-Carboxyl-4'-Diethylamino-2'-Hydroxy Benzophenone (2)

The compound **2** was prepared by using reported procedure [17] (Scheme 2) in good yields (70 %); melting point-202 °C.



Scheme 1 Synthesis of N-methyl-2-pyrrolidonium hydrogen sulphate (1)

Scheme 2 Synthesis of 2carboxyl-4'-diethylamino-2'hydroxy benzophenone (2)



General Procedure for Synthesis of Rhodol Derivatives 3a-3c

A solution compound **2** (1 g, 3.2 mmol) and **a-c** (3.2 mmol, 1 eq.) in the solvent (IL or MSA) (10 mL) was stirred at 85 °C under N₂ atmosphere for 4–15 h. The hot reaction mixture was subsequently poured onto ice cold water (50 vol.). The obtained solid was isolated by filtration, dried and purified by silica gel column chromatography using methanol (2 to 5 %) in chloroform as the eluent. (Scheme 3).

N-(7-Benzoyl-9-(2-Carboxyphenyl)

-6-Hydroxy-3H-Xanthen-3-Ylidene) -N-Ethylethanaminium (3a)

Melting point: 212 °C;

¹H NMR (500 MHz, dmso-d6) δ 8.15 (d, J = 7.7 Hz, 1H), 7.80–7.71 (m, 1H), 7.71–7.64 (m, 1H), 7.61 (d, J = 6.7 Hz, 2H), 7.55 (d, J = 6.2 Hz, 1H), 7.41 (s, 3H), 7.28 (s, 1H), 7.21 (s, 2H), 7.14 (t, J = 10.3 Hz, 2H), 3.70 (q, J = 5.0 Hz, 4H), 1.21 (t, 6H).

¹³C NMR (126 MHz, dmso-d6) δ 159.3, 159.0, 158.7, 158.3, 118.7, 116.4, 114.2, 111.7, 39.1, 38.6, 18.4, 39.1, 38.6.

FTIR (KBr-cm⁻¹): 3420 (OH/COOH), 1761.48 (lactone), 1609, 1356, 675–870.

Mass m/z: 492 (M⁺), 493 (M + 1).

Elemental analysis:

Scheme 3 Synthesis of rhodol

derivatives (3a-3c)

Calculated: C, 72.7134; H, 5.3980; N, 3.2614; O, 18.6271. Found: C, 72.7211; H, 5.3890; N, 3.2615; O, 18.6295.

N-(7-Acetyl-9-(2-Carboxyphenyl)

-6-Hydroxy-3H-Xanthen-3-Ylidene)-N-Ethylethanaminium (**3b**)

Melting point: 214 °C;

¹H NMR (500 MHz, dmso-d6) δ 8.21 (d, J = 8.5 Hz, 1H), 7.83 (t, J = 7.4 Hz, 1H), 7.77 (t, J = 7.1 Hz, 1H), 7.47 (s, 1H), 7.42 (d, J = 7.4 Hz, 1H), 7.21 (s, 1H), 7.18 (d, J = 11.4 Hz, 1H), 7.14 (s, 1H), 7.07 (d, J = 9.4 Hz, 1H), 3.69 (q, J = 7.1 Hz, 4H), 2.45 (s, 3H), 1.19 (t, J = 7.1 Hz, 6H);

¹³C NMR (126 MHz, dmso-d6) δ 200.9, 162.0, 156.2, 152.2, 149.8, 136.1, 132.1, 130.7, 129.0, 126.8, 125.2, 124.5, 119.7, 109.4, 104.2, 97.6, 44.2, 39.8, 39.6, 39.5, 29.1, 12.7;

FTIR (KBr-cm⁻¹): 3429(OH/COOH), 1601, 1353, 764; **Mass** *m*/**z**: 429 (M⁺), 430 (M + 1).

Elemental analysis:

Calculated: C, 75.7489; H, 5.1265; N, 2.8496; O, 16.2750. Found: C, 75.7499; H, 5.1288; N, 2.8499; O, 16.2749.

N-(9-(2-Carboxyphenyl)

-7-Formyl-6-Hydroxy-3H-Xanthen-3-Ylidene)-N-Ethylethanaminium(**3c**)

Melting point: > 350 °C;

¹H NMR (500 MHz, dmso-d6) δ 8.21 (d, J = 7.6 Hz, 1H), 7.84 (t, J = 8.0 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H), 7.57 (s, 1H), 7.43 (d, J = 7.4 Hz, 1H), 7.12 (m, 4H), 3.68 (q, J = 13.5, 7.1 Hz, 4H), 1.18 (t, J = 7.1 Hz, 6H);



IL=Ionic Liquid [NMP]⁺[HSO4]⁻ MSA=Methane sulphonic acid ¹³C NMR (126 MHz, dmso-d6) δ 167.6, 159.3, 159.0, 158.7, 158.4, 118.8, 116.5, 114.2, 111.9, 46.8, 37.0, 12.5;
 FTIR (KBr-cm⁻¹): 3435(-OH/COOH), 1598, 1383,

1108; Mass m/z: 430 (M^+), 432 (M + 1).

Elemental analysis:

Calculated: C, 69.5970; H, 4.9061; N, 3.2465; O, 22.2504. Found: C, 69.5988; H, 4.9059; N, 3.2470; O, 22.2511.

Recyclability of Ionic Liquid, N-Methyl-2-Pyrrolidonium Hydrogen Sulphate (1)

The recyclability study was carried out for the compound **3a**, as representative rhodol. After the completion of the reaction as indicated by TLC, the reaction mixture was cooled to r. t. and then poured on to the ice cold water and precipitated solid was separated by filtration under vacuum. Water was then removed from the filtrate under vacuum using rotary evaporator and the reddish viscous liquid obtained was used for the next cycle without any further purification. The same procedure was then repeated for the next two cycles.

Computational Strategy

The present calculations include the optimization of the dyes in the ground (S_0) and first excited (S_1) state in various solvents. Vertical excitation and emissions were evaluated by single point energy (TD) calculations from S_0 and S_1 optimized geometries, respectively [18]. Present calculations were accomplished using of the Gaussian 09 program package [19]. The geometries of the dyes in their S₀ state were optimized using DFT method [20]. The popular hybrid functional, B3LYP, (the B3LYP combines Becke's three parameter exchange functional (B3) [21] with the non-local correlation functional by Lee, Yang and Parr (LYP) [22] in combination with the basis set 6-31G(d) is used in both, DFT and TD-DFT methods for all the atoms. The vertical excitation energies and oscillator strengths were calculated for the first twenty $S_0 \rightarrow S_1$ transitions at the optimized ground (S₀) state equilibrium geometries by using TD-DFT with the same hybrid functional and basis set [23-27]. To obtain their lowest energy geometries which correspond to the emissive state the low-lying first singlet excited states (S_1) of the dyes were relaxed using the TD-DFT. The emission wavelengths and oscillator strengths were gained for the first ten $S_1 \rightarrow S_0$ transitions at the optimized excited state equilibrium geometries by using the TD-DFT at B3LYP/6-31G(d) level [15, 27, 28]. All the computations in the different solvents were carried out using the Self-Consistent Reaction Field (SCRF) under the Polarisable Continuum Model (PCM) [29, 30].

Results and Discussion

Choice of Solvent-Catalyst

The synthesis of the dyes 3a to 3c were performed using two different solvent-catalyst systems, IL and MSA, and results such as reaction time, and percent yields are summarized in Table 1. It was observed that at 85 °C both in IL (10 mL) and MSA (10 mL) the complete conversion of the starting materials is observed but in IL reaction proceeds faster compared to the MSA with superior yields of the desired products (Table 1). Also the formation of 3c both in IL and MSA systems took place shorter time compared to 3a and 3b owing to lower electron withdrawing effects of carboxylic acid group in c compared to that of ketone in a and b (Scheme 3).

Recyclability Study

In organic synthesis recyclability or reusability of solventcatalyst is a very important factor to make the process economical and environment friendly. We have studied the ability of ionic liquid to recycle without purification for the synthesis of novel rhodol derivative **3a** and results are summarized in Table 2. From Table 2 it is seen that the solvent, IL can be recycled up to 4 cycles without considerable loss in its reactivity which makes the process economical and eco-friendly. Thus the ionic liquid ($[NMP]^+[HSO_4]^-$) is a good candidate as a solvent-catalyst system for the formation of rhodafluors under study.

Photophysical Properties

The photophysical properties of the rhodafluors, **3a-3c** such as absorption maxima, emission maxima, molar absorptivity, oscillator strength, transition dipole moments and quantum yields of fluorescence, etc. in different solvents were investigated and summarized in Table 3. The normalized absorption and emission spectra of the dyes **3a-3c** representative solvent (water) is shown for illustration in Fig. 2 and in different solvents is shown in Figs. S1 to S3 (supporting information).

 Table 1
 Optimization of reaction conditions for synthesis of the rhodafluors (3a-c)

Sr. no.	Compound	Catalyst/solvent	Yield (%)	Time (h)	Temperature (°C)
1	3a	([HNMP] ⁺ [HSO ₄] ⁻)	65	13.5	85
		MSA	49	15	85
2	3b	$([HNMP]^+[HSO_4]^-)$	68	12.5	85
		MSA	53	15	85
3	3c	$([HNMP]^+[HSO_4]^-)$	65	3.5	85
		MSA	52	4.0	85

Cycle no.	Yield (%)		
Fresh	10	93	
1	9.4	91	
2	8.9	88	
3	8.6	84	
4	8.0	79	

 Table 2
 Recyclability study of ionic liquid ([HNMP]⁺[HSO4]⁻)

aprotic solvents such as DMF and DMSO because lactone form predominates over carboxylate form in aprotic solvents. The values of oscillator strength and transition dipole moments follow the similar trend as that of molar absorptivity being highest in water for the dyes **3a-3c**. The compounds **3a-3c** show good quantum yields of fluorescence in different solvents ranging from 0.44 to 0.89.

Effect of Change in pH on Photophysical Properties of the Dyes 3a-3c

From Table 3 and Figs. S1 to S3 it is seen that the dyes **3a**-**3c** absorbs at around 518 nm to 539 nm with no or little effect of change in polarity of microenvironment and emits at around 543 nm to 573 nm in different solvents. The emission maxima in case of all the dyes are influenced more due to change in solvent polarity compared to the absorption maxima and show positive solvatochromism suggest that the dyes **3a-3c** in its excited state are more polar and thus more polar solvents provide the stability to polar forms leading to the red shift in respective emission maxima.

From Table 3 it is seen that the dyes **3a-3c** possess the highest values of molar absorptivity in water followed in methanol. Dyes shows poor values of molar absorptivity in

The position and intensity of the absorption maxima of the dyes **3a-3c** were found to be very sensitive towards change in the pH of microenvironment and it is expected that the dyes **3a-3c** appear in three different forms (A, B and C, Fig. 3) depending on the pH of surrounding media. Thus we observed the changes in absorption peaks of the dyes **3a-3c** with respect to change in pH of the microenvironment and results are illustrated in Figs. 4-6, respectively. The pH of the medium determines as to which form predominates over the other. When the dyes were treated/ dissolved in PBS buffer of different pH it was observed that at certain pH there is sudden enhancement in the absorption intensity of the dyes **3a-3c**.

 Table 3
 Photophysical properties of rhodol derivatives 3a, 3b and 3c, in various solvents

Solvent	$\lambda_{abs}{}^anm$	$FWHM^b cm^{-1}$	$\lambda_{em}^{\ \ c}$ nm	$\Delta \ ^{\rm d} \ \rm cm^{-1}$	$\epsilon_{max}^{ \ e} \ M^{-1} \ cm^{-1}$	$\int \varepsilon(\vartheta) dv^{\rm f} / 10^8 { m M}^{-1} { m cm}^{-2}$	f ^g	$\mu_{eg}{}^h$	$\varphi_{\rm fl}{}^i$
Dye 3a									
Water	533	1325	564	1031	84,716	1.89	0.8297	9.70	0.70
MeOH	528	1297	558	1018	38,221	0.70	0.3073	5.88	0.66
EtOH	526	1399	560	1154	10,835	0.18	0.0790	2.97	0.80
DMSO	533	1942	573	1310	6895	0.15	0.0659	2.73	0.55
Dye 3b									
Water	536	1367	566	989	102,176	1.99	0.8736	9.98	0.74
MeOH	534	1415	564	996	5854	0.18	0.0790	3.00	0.45
EtOH	533	1868	564	1031	6198	0.14	0.0615	2.64	0.67
DMF	539	2044	570	1009	1549	0.13	0.0571	2.56	0.44
Dye 3c									
Water	529	2774	555	1176	53,484	1.66	0.7287	7.56	0.45
MeOH	520	1903	543	815	4843	0.18	0.0790	2.50	0.88
EtOH	518	2103	543	889	1954	0.07	0.0307	1.56	0.89

^a Wavelength absorption maximum

^b Full width at half absorption maxima

^c Wavelength emission maximum

^d Stokes shift

^e Molar absorptivity at absorption maximum

^f Integrated area of absorption coefficient

g Oscillator strength

h Transition dipole moment

ⁱ Quantum yield of fluorescence

Fig. 2 Normalized absorption (*solid lines*) and emission (*dashed lines*) spectra of the dyes **3a-3c** in water



From Fig. 4 it is seen that at pH 4 the dye **3a** show dual absorptions with almost similar intensity, at 340 nm and 533 nm, corresponds to form A and B or C. As the pH increases there is enhancement in intensity of the band at 533 nm and at pH change from 5 to 6 the dye **3a** shows 4 folds increase in the absorption intensity at its absorption maxima (533 nm) and after pH 6 there is no further considerable change in the absorption intensity (Fig. 4). On the other hand it was observed that there is a decrease in the intensity of absorption band at 340 nm, which corresponds to the form A, with the increase in pH (Fig. 4). Thus complete opening of spiro ring occurs at pH 6, conversion of form A to form B or C (Fig. 3).

Similarly the dye **3b** shows 2.5 fold increase in its absorption intensity when pH changes from 5 to 7 with no further change in the intensity upon increasing the pH (Fig. 5) and the dye **3c** show gradual increase in the intensity after pH 7 till pH 12 (Fig. 6).

The dyes **3a-3c** show different response towards change in the pH that could be attributed to the electron withdrawing ability of the substituent present on the phenol ring of the fluorophore (Fig.3). As acetyl substituent in dye **3a** owing to its highest electron withdrawing ability compared to benzoyl and carboxyl groups in **3b** and **3c** respectively, facilitates complete opening of the lactone to carboxylate at relatively lower pH.

DFT and TD-DFT Studies

The density functional theory (DFT) [20] and time dependent density functional theory (TD-DFT) [20] with B3LYP/6-31G(d) [20–22] level were used to get more understanding of the structural, and photophysical properties of rhodafluors under study. The unconstrained geometries of the dyes in their S_0 and S_1 states in vacuum as well as in different solvents were optimized by DFT using the Becke's three-parameter functional [21] hybridized with the Lee–Yang–Parr correlation functional [22] and the 6-31G(d,) basis set [23, 24, 31].

Optimized Geometries of the Dyes 3a-3c

The TD-DFT optimized geometries and main geometrical parameters of the rhodol derivatives (dyes **3a-3c**) for keto form (Form B, Fig. 3) in its S_0 and S_1 states are shown in Figs. 7-9



Dye 3a; R = -Ph, **Dye 3b**; R= -Me **Dye 3c**; R= -OH

Fig. 3 Possible forms of rhodafluors (a-c) at different pH conditions



Fig. 4 Effect of change in pH on absorption intensity of compound 3a in PBS buffer

and collected in Table S1. From Figs. 7-9 it is seen that the main rhodol chromophore (Figs. 7-9) possesses perfectly planar arrangement thus allowing effective *p*-orbital overlap throughout, N1 to O1 and O1 to O2.

In the dye **3a** (Fig. 7) in S₀ state the phenyl substituent at C6 is oriented with main chromophore almost orthogonally making a dihedral angle of 88.4° but in first excited (S₁) it becomes twisted from its orthogonal arrangement by 22° making final dihedral angle of 66.4°. The benzoyl substituent at C9 show twisting from planar arrangement by 48.2° in S₀ state but the twisting decreases by 16.7° in S₁ state making dihedral angle of 31.3°. From Fig. 7 it is seen that there occurs elongation of the bonds in S1 state compared to the S₀ in the main chromophore, except C5-C6, C7-C8 and C9-C10, suggests the polarization of the chromophore in its excited state.



Fig. 5 Effect of change in pH on absorption intensity of compound **3b** in PBS buffer



Fig. 6 Effect of change in pH on absorption intensity of compound 3c in PBS buffer

The dyes **3b** and **3c** (Figs. 8 and 9) in its S_0 and S_1 states show similar observations except the acetyl and carboxy substituents in the dyes **3b** and **3c**, respectively, possesses perfectly planar arrangement with main chromophore making effective *p*-orbital overlap supports the red shifted absorption and emission of the dye **3b** compared to that of the dyes **3a** and **3c** (Table 3).

TD-DFT Absorption and Emissions

The TD-DFT absorption and emission energies, major electronic configurations, and transition nature of the selected S_0 and S_1 states with large oscillator strengths (*f*) along with respective experimental values such as absorptions and emissions of keto forms of the dyes **3a-3c** in different solvent media for comparison are listed in Table 4.

For the dyes 3a-3c in all solvents studied (Table 4) the vertical excitations originates from the HOMO to LUMO with good orbital contributions and oscillator strengths. Table 4 revealed that the TD-DFT absorptions for the dyes 3a-3c are centered around 474.1 nm to 481. 9 nm with 8.3 to 10.8 % deviations from observed values of absorptions in different solvents with very good oscillator strengths (0.7737 to 0.9142). From Table 4 it is seen that the TD-DFT account for emission of the rhodafluors (3a-3c) fairly accurately and are centered around 532.0 nm to 556.0 nm with 1 % to 5 % deviations from the observed values of emission maxima. TD-DFT emissions originated from the LUMO to HOMO transitions with good oscillator strengths supports the good quantum yields of fluorescence of the dyes 8.3 to 3a-3c. From Table 4 it is seen that the TD-DFT also accounts for the red shifted absorption and emission maxima of the dye 3b compared to that of the dyes 3a and 3c.





TD-DFT Analysis of FMOs

In order to gain detailed insight on electronic and photophysical properties of the rhodafluors under investigation their frontier molecular orbitals (FMOs), particularly the HOMO and LUMO were examined and respective counter

plots are shown in Fig. 10. From Fig. 10 it is seen that in HOMO the major portion of the charge density is localized on amine part of the chromophore. The charge density at amine part in HOMO is transferred to keto part of the chromophore in LUMO supports the formation of zwitter ionic form C (Fig. 3).





Table 4	TD-DFT B3LYP/6-31G(d)	calculated absorr	otion and emission	parameters of the dv	es 3a to 3c in different solvents
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Solvent	$\lambda_{abs}{}^a$	$\lambda_{abs}{}^{b}$	f^c	$\% D^d$	Major orbital contribution	$\lambda_{em}^{ e}$	$\lambda_{em}{}^{f}$	$f^{\rm g}$	$\% D^{\rm h}$	Major orbital contribution
Dye 3a										
Water	533	475.4	0.8878	10.8	$\mathrm{H} \rightarrow \mathrm{L} \; (94.1 \; \%)$	564	537.7	0.6254	4.66	$L \rightarrow H (92.2 \%)$
MeOH	528	474.9	0.8815	10.0	$\mathrm{H} \rightarrow \mathrm{L} \ (94.0 \ \%)$	558	539.8	0.6084	3.26	$L \rightarrow H (91.9 \%)$
EtOH	526	475.8	0.8909	9.54	$\mathrm{H} \rightarrow \mathrm{L} \; (94.2 \; \%)$	560	542.1	0.6110	3.20	$L \rightarrow H (92.1 \%)$
DMSO	533	477.9	0.9142	10.3	$\mathrm{H} \rightarrow \mathrm{L} \ (94.5 \ \%)$	570	541.4	0.6452	5.02	$L \rightarrow H (92.7 \%)$
Dye 3b										
Water	537	478.6	0.8063	10.9	$\mathrm{H} \rightarrow \mathrm{L} \; (95.8 \; \%)$	566	550.4	0.4794	2.76	$L \rightarrow H (93.6 \%)$
MeOH	536	478.3	0.7993	10.8	$\mathrm{H} \rightarrow \mathrm{L} \; (95.7 \; \%)$	564	553.2	0.4662	1.91	$L \rightarrow H (93.6 \%)$
EtOH	534	479.4	0.8086	10.2	$\mathrm{H} \rightarrow \mathrm{L} \; (95.9 \; \%)$	564	535.6	0.5490	5.04	$L \rightarrow H (93.8 \%)$
DMF	539	481.9	0.8365	10.6	$\mathrm{H} \rightarrow \mathrm{L} \; (96.2 \; \%)$	570	556.0	0.4976	2.46	$L \rightarrow H (94.3 \%)$
Dye 3c										
Water	521	474.3	0.7815	8.97	$H \rightarrow L (95.8 \%)$	555	532.0	0.5175	4.14	$L \rightarrow H (93.6 \%)$
MeOH	520	474.1	0.7737	8.82	$\mathrm{H} \rightarrow \mathrm{L} \ (95.7 \ \%)$	543	534.8	0.5010	1.51	$L \rightarrow H (93.4 \%)$
EtOH	518	475.3	0.7825	8.25	$\mathrm{H} \rightarrow \mathrm{L} \ (95.8 \ \%)$	543	537.5	0.5040	1.01	$L \rightarrow H (93.6 \%)$

^a Experimental absorption maximum

^b TD-DFT absorption maximum

^c Oscillator strength of vertical excitation

^d Deviation in TD-DFT absorption maximum from the experimental absorption maximum

^eExperimental emission maximum

^fTD-DFT emission maximum

^g Oscillator strength of vertical emission

^h Deviation in TD-DFT emission maximum from the experimental emission maximum



Fig. 10 Energy level and electron density distribution of frontier molecular orbitals of dyes 3a-3c in water solvent, calculated by B3LYP/6-31G(d) level of theory (The orbital diagrams were plotted with the contour value of 0.02 a. u)

TD-DFT Dipole Moments

Photon absorption by chromophore in its S_0 state is responsible for its excitation to the S_n (n is 1, 2, 3, and so on) states associated with redistribution of the electron density, which brings the change in the dipole moment in the S_n state. Dipole moments of the molecules in the S_1 state relative to that in S_0 in different microenvironments are useful to extract parameters like molecular polarizability and to evaluate the electron density distribution in the S_1 and T_1 states.

From Table 5 it is seen that, for the dyes **3a-3c** the dipole moments in S₁ state is higher than that of S₀ state ($\mu_e > \mu_g$), suggesting the more polar excited state. Also for all the dyes **3a-3c** dipole moments both in S₀ and S₁ states, increases with increase in the solvent polarity indicates the formation of more polarized state with increase in solvent polarity being highest in water, followed by DMSO/DMF, then MeOH and lastly EtOH (Table 5).

Conclusion

In this paper we report green protocols for synthesis of three novel rhodol derivatives in good yields. Recyclability of the

Table 5TD-DFT B3LYP/6-31G(d) calculated dipole moments of thedyes 3a to 3c in ground and first excited states in different solvents

Solvent	$\mu_{\rm g}{}^a$	μ_e^b	$\Delta \mu_{eg}^{\ \ c}$	
Dye 3a				
Water	18.46	19.90	1.44	
MeOH	18.21	19.68	1.47	
EtOH	18.08	19.57	1.49	
DMSO	18.34	19.79	1.45	
Dye 3b				
Water	19.28	21.30	2.03	
MeOH	19.01	21.07	2.06	
EtOH	18.88	20.04	1.17	
DMF	19.07	21.12	2.06	
Dye 3c				
Water	19.28	20.46	1.19	
MeOH	19.00	20.23	1.23	
EtOH	18.86	20.12	1.26	

^a TD-DFT dipole moment in S₀ state

^b TD-DFT dipole moment in S₁ state

^c Difference between the dipole moments in S₀ and S₁ states

catalyst-solvent, mild reaction conditions, easy workup procedures are some of the striking features of present protocols. The results of pH study reveals that the new rhodafluors can be used as efficient pH probes. The structural and photophysical properties of the dyes under study are rationalized by means of DFT and TD-DFT.

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