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# Intramolecular excited charge transfer, radiative and radiationless charge recombination processes in donor–acceptor imidazole derivatives

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ABSTRACT

Solvent-dependent electronic structure of the selected donor (D)–acceptor (A) derivatives of imidazole containing naphthyl as an electron acceptor fragment in the fluorescent charge transfer (CT) states has been investigated. The mechanism of the radiative charge recombination CT → $S_0$ is discussed in terms of the Mulliken–Murrell model of the CT complexes and the Marcus theory of photoinduced electron transfer (ET). Solvatochromic effects on the spectral position and profile of the stationary fluorescence spectra clearly indicate the CT character of the emitting singlet states of all the compounds studied both in a polar and a non polar environment. An analysis of the CT fluorescence leads to the quantities relevant for the electron transfer in the Marcus inverted region. The fluorescence rate constants ($k_r$), corresponding transition dipole moments ($M$) and their solvent polarity dependence indicate that the electronic coupling between the emitting $^1$CT state and the ground state is a governing factor of the radiative transitions. The relatively large values of $M$ indicate a nonorthogonal geometry of the donor and acceptor subunits in the fluorescent states.



## 1. Introduction

The wide investigations of the intramolecular electron transfer (ET) in donor (D)–acceptor (A) compounds such as carbazol-9-yl derivatives of aromatic nitriles [1] and aryl or hetero aryl derivatives of aromatic amines [2] suggest a possibility to predict the photophysical behavior of a particular D–A molecule from the properties of the individual chromophores as far as the electronic interactions between the lowest excited charge transfer state CT and the ground state $S_0$ ($V_0$) and/or the locally excited states LE, localized either in the acceptor ($V^A_{1,2}$) or in the donor ($V^D_{1,3}$) respectively, are taken into account. A similar approach can be applied to describe the properties of the singlet CT states e.g., the transition dipole moments for the CT absorption ($^1$CT ← $S_0$) and the fluorescence ($^1$CT → $S_0$) as well as the characteristics of the triplet $^3$CT states [3] (e.g., the zero-field splitting parameters).

The study of the intramolecular ET reactions is to identify structural elements that promote electronic coupling between an electron donor and an acceptor is a challenging one. The application of different models [4–6] used to determine the electronic matrix elements from the solvent polarity effects on the electronic transition dipole moments of the CT emission ($M_{flu}$) [7,8] and the CT absorption ($M_{abs}$) [2]. The appropriate values of the electronic coupling elements are mainly determined by the interactions between the atoms forming the bond A–D can be theoretically predicted following the formalism proposed by Dogonadze et al. [9,10]. Neglecting contributions from the $\sigma$ orbitals, one can obtain for $\pi$-electronic systems.

$$V_0 = C^A_{LUMO} C^D_{HOMO} \beta_{AD} \cos(\Theta_{A-D}) + \text{const.}, \quad (1)$$

$$V^A_{1,3} = C^A_{HOMO} C^D_{HOMO} \beta_{AD} \cos(\Theta_{A-D}) + \text{const.}, \quad (2)$$

$$V^D_{1,3} = C^A_{LUMO} C^D_{LUMO} \beta_{AD} \cos(\Theta_{A-D}) + \text{const.}, \quad (3)$$

where $\Theta_{A-D}$ denotes the angle between the planes of the acceptor and donor subunits and $C_{HOMO}$ and $C_{LUMO}$ are the LCAO co-efficients (as obtained for the individual chromophores) of the $2p_Z$ atomic orbitals (where $z$ is the axis perpendicular to the acceptor or donor rings) of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) located on the atoms forming the A–D bond. $\beta$ is the resonance integral for these AD atoms and constant is related to the electronic interactions between the remaining pairs of atoms in the D–A molecule (this contribution is usually small and negligible). Expressions 2 and 3 assume that the $^1$LE state is mainly described by a configuration corresponding to the HOMO → LUMO excitation (e.g., $^1L_a$ state in Platt's notation).

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In this work, we have used the Lippert solvent parameter ($\Delta f$), the normalized $E_T(30)$ polarity scale and the multi parameter Kamlet–Taft and Catalan solvent scales to describe the solvent effect on the fluorescence emission and Stokes shift of imidazole derivatives. The influence of solvents on the photophysical properties of the synthesized molecules in terms of $hc\tilde{\upsilon}_{abs}^{vac}$, $hc\tilde{\upsilon}_{flu}^{vac}$ and $(hc\tilde{\upsilon}_{abs}^{vac} - hc\tilde{\upsilon}_{flu}^{vac})$ with solvent polarity function have also been addressed. A photophysical study on bioactive molecule with phenolic function hydroxyl 2-napthylimidazole is of our interest, it exhibit excited state intramolecular proton transfer (ESIPT) and density functional theory (DFT) calculations support the ESIPT in hydroxyl 2-naphthylimidazole derivative. We have also report the elegant catalytic synthesis, characterization and solvatochromism of imidazole molecules with naphthyl as the acceptor units. Single crystal X-ray diffraction (XRD) supports the structure of the newly synthesized 1-(4-methoxyphenyl)-2-(4-naphthalen-1-yl)-4,5-diphenyl-1H-imidazole. The presented results are based on a study of the solvent effects on the spectral position of absorption and fluorescence spectra as well as on the CT emission quantum yields and excited state depopulation kinetics.

## 2. Experimental

### 2.1. Spectral measurements

The $^1$H and proton decoupled $^{13}$C NMR spectra imidazole derivatives **1–4** were recorded at room temperature using a Bruker 400 MHz NMR spectrometer. The mass spectra of the samples were obtained using a thermo Fischer LC-mass spectrometer in FAB mode. The UV–vis absorption and fluorescence spectra were recorded in all solvents with PerkinElmer Lambda 35 spectrophotometer and PerkinElmer LS55 spectrofluorimeter, respectively. Fluorescence lifetime measurements were carried out with a nanosecond time correlated single photon counting (TCSPC) spectrometer Horiba Fluorocube-01-NL lifetime system with Nano LED (pulsed diode excitation source) as the excitation source and TBX-PS as detector. The slit width was 8 nm and the laser excitation wavelength was 260 nm. The fluorescence decay was analyzed using DAS6 software. The quantum yield for all the imidazoles were measured in dichloromethane using coumarin 47 in ethanol as the standard [11a–c].

### 2.2. Cyclic voltammetry

The cyclic voltammetry analyses were performed with CHI 630A potentiostap-electrochemical analyzer at scan rate of 100 mV s$^{-1}$ using 0.1 M tetra-(*n*-butyl)-ammonium hexafluorophosphate as supporting electrolyte with $Ag/Ag^+$ (0.01 M $AgNO_3$) as the reference electrode and Pt electrode as the working electrode under nitrogen atmosphere at room temperature.

### 2.3. Computational details

The quantum chemical calculations were performed using the Gaussian-03 [12] package. Computations of the vertical excitations, difference density plots and optimization of the ground and excited states were performed using density functional theory (DFT) and time-dependent DFT (TD-DFT) using B3LYP/6-31G (d,p) basis set, respectively. The ground and excited states HOMO and LUMO frontier orbital's of imidazole derivatives were calculated by both DFT and TD-DFT methods at the B3LYP/6-31 (d,p) level.

### 2.4. General procedure for the facile and rapid synthesis of 2-naphthyl imidazoles by $InF_3$

A mixture of corresponding aldehyde (1 mmol), benzil (1 mmol), corresponding aniline (1 mmol), ammonium acetate (1 mmol) and $InF_3$ (1 mol %) was stirred at solvent-free conditions at 80 °C. The progress of the reaction was monitored by TLC (Scheme 1). After completion of the reaction, the mixture was cooled, dissolved in acetone and filtered. The product was purified by column chromatography using benzene: ethyl acetate (9:1) as the eluent.

#### 2.4.1. Catalytic activity of indiumtrifluoride

Initially, we have carried out the condensation reaction in the presence of $InF_3$ (1 mol%), naphthaldehyde (1 mmol), ammonium acetate (1 mmol) and arylamine (1 mmol) in different solvents such as water, ethanol, methanol, chloroform, and acetonitrile under refluxing and also in solvent-free conditions at 80 °C. From these experiments, it was clearly demonstrated that the solvent-free condition is the best for imidazole synthesis. In the absence of catalyst under solvent-free conditions, at room temperature for 24 h, led to very poor yield (12%). To enhance the yield of the desired product, the temperature of the reaction was increased to 200 °C, but no appreciable increment in the product yield was observed. We found that presence of a catalytic amount of $InF_3$ and solvent-free are the best conditions for this synthesis; maximum yield (82%) was obtained on loading with 1 mol% of $InF_3$ at 80 °C with 30 min. Moreover, $InF_3$ can be recovered and reused several times without significant loss of activity. High product yields, shorter reaction time, low catalyst loading and easy work-up procedure, make this procedure quite simple and more convenient. Our methodology could be a valid contribution to the existing processes of imidazole synthesis.

#### 2.4.2. 8-(1,4,5-Triphenyl-1 H-imidazol-2-yl)naphthalene-2-ol (**1**)

M.p. 187 °C, anal. calcd. for $C_{31}H_{22}N_2O$: C, 84.91; H, 5.06; N, 6.39; O, 3.65. Found: C, 84.89; H, 5.02; N, 6.35; O, 3.62. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.94 (d, $J$ = 8.4 Hz, 1H), 7.04 (q, $J$ = 4.6 Hz, 3H), 7.21–7.32 (m, 10H), 7.47 (t, $J$ = 5.6 Hz, 2H), 7.67 (d, $J$ = 7.6 Hz, 2H), 7.80 (d, $J$ = 7.2 Hz, 2H), 8.19 (d, $J$ = 6.4 Hz, 1H), 12.99 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 124.72, 126.20, 126.32, 126.70, 126.76, 127.69, 127.88, 127.93, 127.99, 128.15, 128.24, 128.39, 128.56, 128.72, 129.38, 129.50, 129.96, 130.87, 131.16, 132.89, 133.73, 134.63, 136.71, 138.30, 146.53. MS: $m/z$ 438[M+].

#### 2.4.3. 2-(Naphthalene-1-yl)-4,5-diphenyl-1-p-tolyl-1H-imidazole (**2**)

M.p. 168 °C, anal. calcd. for $C_{32}H_{24}N_2$: C, 88.04; H, 5.54; N, 6.42. Found: C, 88.01; H, 5.50; N, 6.39. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.75(d, $J$ = 7.2 Hz, 2H), 6.81 (d, $J$ = 7.6 Hz, 1H), 7.25 (m, 6H) 7.47(d, $J$ = 6, 3H), 7.64 (d, $J$ = 7.2 Hz, 2H), 7.80 (s, 2H), 8.18(t, $J$ = 7.2 Hz, 1H), 2.15 (s, 3H), 1.67 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 21.03, 124.64, 126.01, 126.32, 126.57, 126.65, 127.51, 127.53, 127.90, 128.07, 128.17, 128.37, 128.44, 129.21, 129.24, 129.38, 129.95, 130.92, 131.10, 132.89, 133.59, 134.00, 134.65, 137.57, 137.98, 146.21. MS: $m/z$ 422 [M+].

#### 2.4.4. 1-(4-Methoxyphenyl)-2-(4-naphthalen-1-yl)-4,5-diphenyl-1H-imidazole (**3**)

M.p. 174 °C, anal. calcd. for $C_{32}H_{24}N_2O$: C, 84.93; H, 5.35; N, 6.19; O,3.54. Found: C, 84.90; H, 5.31; N, 6.16; O,3.52. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.53(d, $J$ = 8.4 Hz, 2H), 6.80 (d, $J$ = 8.4 Hz, 2H), 7.29 (m, 6H), 7.47(t, $J$ = 6, 2H), 7.64 (d, $J$ = 7.2 Hz, 2H), 7.80 (bs, 2H), 8.17(d, $J$ = 4.8 Hz, 1H), 3.63 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 55.21, 124.66, 125.08, 126.02, 126.28, 126.58, 126.65, 127.50, 127.91, 128.09, 128.17, 128.41, 128.46, 128.63, 128.86, 129.24, 129.38, 129.44, 130.09, 130.90, 131.09, 132.88, 133.60, 134.62, 137.88, 146.34. MS: $m/z$ 452 [M+].