



## Synthesis and photophysical studies of oxazole rings containing compounds as electron accepting units

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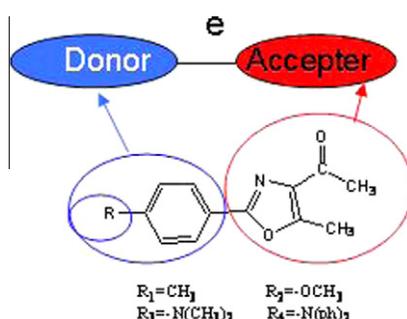
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### HIGHLIGHTS

- ▶ Four compounds with oxazole and benzene rings have been synthesized.
- ▶ The ICT was observed with the enhancing of the electron-donor ability.
- ▶ 5-Methyl-2-(*p*-*N,N*-diphenylamino phenyl)-4-acetyl oxazole shows obvious ICT.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A series of oxazole derivatives, 5-methyl-2-(*p*-methylphenyl)-4-acetyl oxazole (MMPAO), 5-methyl-2-(*p*-methoxyphenyl)-4-acetyl oxazole (MOPAO), 5-methyl-2-(*p*-*N,N*-dimethylamino-phenyl)-4-acetyl oxazole (MDMAPAO) and 5-methyl-2-(*p*-*N,N*-diphenylaminophenyl)-4-acetyl oxazole (MDPAPAO) have been synthesized and studied to compare their photophysical properties. The UV–visible absorption spectra of MDMAPAO and MDPAPAO are bathochromatically shifted as compared to that of MMPAO and MOPAO. The fluorescence emission of MDPAPAO is very sensitive to the polarity of solvents. The magnitude of change in the dipole moment was calculated using the Lippert–Mataga equation. MDPAPAO shows the highest change in the dipole moment ( $\Delta u = 13.3D$ ) than that of the other three oxazole derivatives. The spectral properties including fluorescence quantum yield and lifetime were determined in solvents with different polarities. MDPAPAO displays the highest fluorescence quantum yield and lifetime, following a bi-exponential fluorescent decay fashion. Our result demonstrates that the excited state of MDPAPAO possesses the property of intramolecular charge transfer.

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### Introduction

Since the first observation of dual emission in *N,N*'-dimethylaminobenzonitrile by Lippert et al. [1], photoinduced intramolecular charge transfer (ICT) has become the object of much interest in the past few decades. ICT is a fundamental process of the excited states

and has formed an indispensable building block of photochemistry [2]. In ICT, a charge separation may result from the transfer of charge from a donor (D) to an acceptor (A) within a pertinent molecule upon photoexcitation. Aromatic compounds, especially those containing five-membered heteroaromatic units, possessing electron donor–acceptor chromophores and exhibiting dual fluorescence are of particular interest because the additional fluorescence is usually associated with the ICT state [3–8]. Among the *p*-conjugated compounds with five-membered heteroaromatic rings, pyrrole and thiophene [9–12] are typical electron-donating units while imidazole [13], thi-

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azole [14,15], triazole [16], oxadiazole [17,18], and thiadiazole [19] usually possess electron-accepting property owing to the electron-withdrawing ability of the imine group. In addition, oxazole possessing the electron-accepting five-membered ring is another good candidate of *p*-conjugated compound.

Oxazoles are considered as an important class of heterocyclic compounds since they have been used as efficient luminophores for liquid and plastic scintillators, laser dyes, organic light-emitting materials and as fluorescent probes for biological systems [20,21]. Oxazoles are associated with anti-bacterial, anti-fungal, anti-inflammatory and anti-tumoral activities and can be used as peptide mimics or enzyme inhibitors [22–24]. The physicochemical and photophysical properties of some oxazole derivatives were extensively studied in the past year because of their potential applications. However, most of the studies only focus on the hydrogen bonding capability of oxazole or the excited state intramolecular proton transfer; unfortunately, their ICT character is not so prominent [25,26]. In order to enhance the ICT character of oxazoles, better electron-donating moiety could be introduced to the oxazoles. In here, some 2-phenyloxazole derivatives such as 5-methyl-2-(*p*-methylphenyl)-4-acetyl oxazole (MMPAO), 5-methyl-2-(*p*-methoxyphenyl)-4-acetyl oxazole (MOPAO), 5-methyl-2-(*p*-*N,N'*-dimethylaminophenyl)-4-acetyl oxazole (MDMAPAO) and 5-methyl-2-(*p*-*N,N'*-diphenylaminophenyl)-4-acetyl oxazole (MDPAPAO) are successfully synthesized and reported. The ICT of these 2-phenyloxazole derivatives were studied in detail and they possess interesting electron-donating groups on their *p*-benzene rings which indeed could enhance their ICT character. The effect of solvent polarity on the absorption and fluorescence emission spectra of the 2-phenyloxazole derivatives was investigated and the charge transfer property of these compounds was systematically studied.

It is well known that fullerene (C<sub>60</sub>) can act as an electron acceptor when interacting with a conjugated heteroaromatic compound as an electron donor. In order to compare the ICT property of the 2-phenyloxazole derivatives, the inter-molecular interaction of MDPAPAO with fullerene (C<sub>60</sub>) was also investigated. The experimental results should provide solid evidence to support the electron-donating ability of MDPAPAO. Finally, it is our wish that these fundamental data could provide valuable information for understanding the ICT character of these new 2-phenyloxazole derivatives.

## Experimental

### Materials

All solvents including cyclohexane, diethyl ether, ethyl acetate, acetonitrile and ethanol of analytical-grade were purchased from Beijing Chemical Plant (Beijing, China). All chemicals and reagents were used as received unless otherwise stated.

### Synthesis of compounds with oxazole ring

Scheme 1 outlines the synthesis routes for the new oxazole derivatives. In essence, *p*-benzaldehyde containing various substituted groups were allowed to react with 3-(hydroxyimino)pentane-2,4-dione in HCl gas saturated with glacial acetic acid at 0–5 °C to obtain the substituted oxazole intermediates [27,28]. The intermediates were reduced to its corresponding target oxazole derivatives by Zn powder in glacial acetic acid for 5 h at 40–50 °C. The reaction mixture was purified by column chromatography on silica gel to obtain 77%, 51%, 24% and 22% yields of MMPAO, MOPAO, MDMAPAO and MDPAPAO, respectively. Their melting points, IR, <sup>1</sup>H NMR and MS data were shown as following:

MMPAO: m.p. 84–85 °C

IR(KBr),  $\nu/\text{cm}^{-1}$ : 1598.9, 1560.3, 1500.5, 1419.5, 825.5, 1678.0, 1647.1, 1174.6, 1382.9.

<sup>1</sup>H NMR,  $\delta$ : 2.40 (s, 3H), 2.60 (s, 3H), 2.71 (s, 3H), 7.30 (d, 2H), 7.29 (d, 2H).

MOPAO: m.p. 86–88 °C

IR(KBr),  $\nu/\text{cm}^{-1}$ : 1614.3, 1598.9, 1502.4, 1458.1, 837.0, 1681.8, 1614.3, 1170.7, 1382.9.

<sup>1</sup>H NMR,  $\delta$ : 2.56 (s, 3H), 2.67 (s, 3H), 3.88 (s, 3H), 6.95 (d, 2H), 7.98 (d, 2H).

MDMAPAO: m.p. 131–133 °C

IR(KBr),  $\nu/\text{cm}^{-1}$ : 1598.9, 1614.3, 1512.1, 1429.2, 815.8, 1674.1, 1357.8.

<sup>1</sup>H NMR,  $\delta$ : 2.58 (s, 3H), 2.66 (s, 3H), 3.04 (s, 3H), 6.74 (d, 2H), 7.89 (d, 2H).

MDPAPAO: m.p. 132–134 °C

IR(KBr),  $\nu/\text{cm}^{-1}$ : 690–710, 730–770, 1500, 1600, 790–840, 1685.7, 1600–1635, 1176.5, 2910–2950.

<sup>1</sup>H NMR,  $\delta$ : 7–8 (m, 14H), 2.2 (s, 3H), 2.8 (s, 3H).

MS, *m/z*: 368.22, 325.11, 42.92, 76.98, 167.11.

### Instrumentation

All UV absorption spectra were recorded on a Shimadzu UV-265 UV–visible absorption spectrophotometer (Tokyo, Japan). Fluorescence spectra were taken on a Hitachi F4500 spectrofluorometer (Tokyo, Japan). Both excitation and emission slits were set at 5 nm. All the experiments are carried out at 20 ± 1 °C. The fluorescence lifetime measurements were performed on an Edinburgh FLS920 fluorescence lifetime spectrometer (Livingston, UK) operating in the time-correlated single photon counting mode. The excitation source was a hydrogen lamp (Edinburgh Instruments). The lifetime values were obtained from the re-convolution fit analysis using a double-exponential decay function of the decay profiles with F900 analysis software. The goodness of fit was evaluated by the reduced  $\chi^2$  value (close to 1 in all case).

### Fluorescence quantum yields

The fluorescence quantum yields were obtained using quinine bisulfate in 0.050 M sulfuric acid as standard and calculated on the basis of Eq. (1) [29,30]:

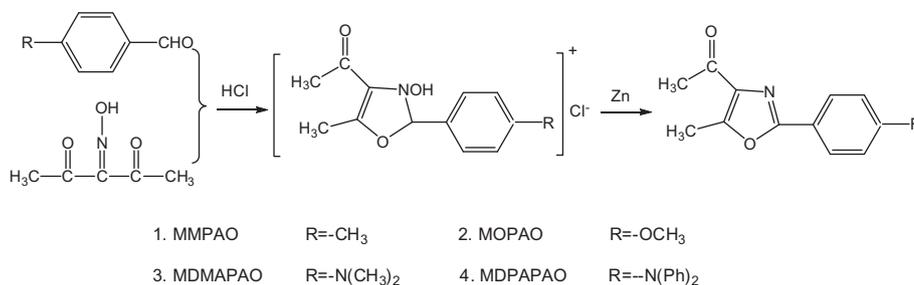
$$\phi_f^u = \phi_f^s \frac{F_u A_s n_u^2}{F_s A_u n_s^2} \quad (1)$$

where *F* represents the corrected fluorescence peak area, *A* is the absorbance at the excitation wavelength, *n* is the refractive index of the solvent used,  $\phi_f$  is the fluorescence quantum efficiency and the superscripts and subscripts 's' and 'u' refer to standard and unknown, respectively.

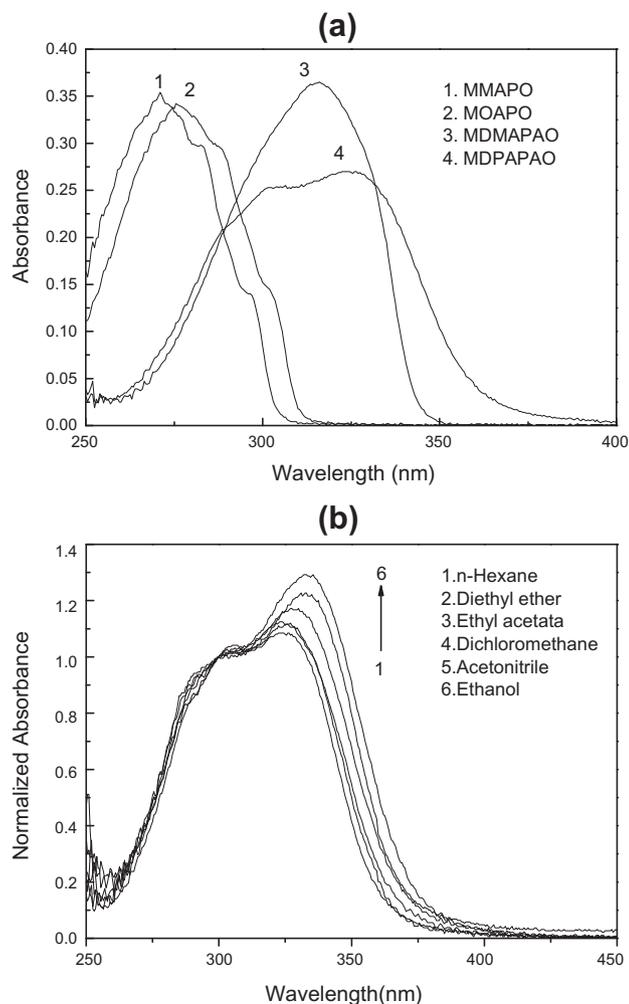
## Results and discussion

### Absorption and fluorescence emission characteristics

Fig. 1a depicts the absorption spectra of MMPAO, MOPAO, MDMAPAO and MDPAPAO in ethyl acetate. All these oxazole compounds display strong absorption bands in UV region with their absorption peak maxima ( $\lambda_{\text{max}}$ ) at 272, 277, 318 and 330 nm, respectively. The  $\lambda_{\text{max}}$  of the oxazole compounds follows the trend: MMPAO < MOPAO < MDMAPAO < MDPAPAO, closely relating to the electron-donating ability of the substituents on the parent oxazole: *p*-methylphenyl < *p*-methoxyphenyl < *p*-*N,N'*-dimethylaminophenyl < *p*-*N,N'*-diphenylaminophenyl. Larger red-shifts in the spectra were observed for MDMAPAO and MDPAPAO as com-



**Scheme 1.** The synthesis routes of MMPAO, MOPAO, MDMAPAO and MDPAPAO.



**Fig. 1.** (a) UV-visible absorption spectrum of MMPAO, MOPAO, MDMAPAO and MDPAPAO in ethyl acetate. The concentrations are 0.15 mM. (b) Normalized UV-visible absorption spectrum of MDPAPAO in *n*-cyclohexane, diethyl ether, ethyl acetate, dichloromethane, acetonitrile, and ethanol.

pared to MMPAO and MOPAO, indicating that the dimethylamino and diphenylamino moieties show stronger electron-donating ability than that of the methyl and methoxy moieties. In addition, the  $\lambda_{\max}$  of the oxazole compounds in other solvents of various polarities such as *n*-cyclohexane, diethyl ether, ethyl acetate, dichloromethane, acetonitrile and ethanol are summarized in Table 1. It was found that the  $\lambda_{\max}$  of MMPAO and MOPAO do not change much with the solvent polarity whereas it is more pronounced for MDMAPAO and MDPAPAO. Fig. 1b shows the absorption spectra of MDPAPAO in organic solvents with different

**Table 1**

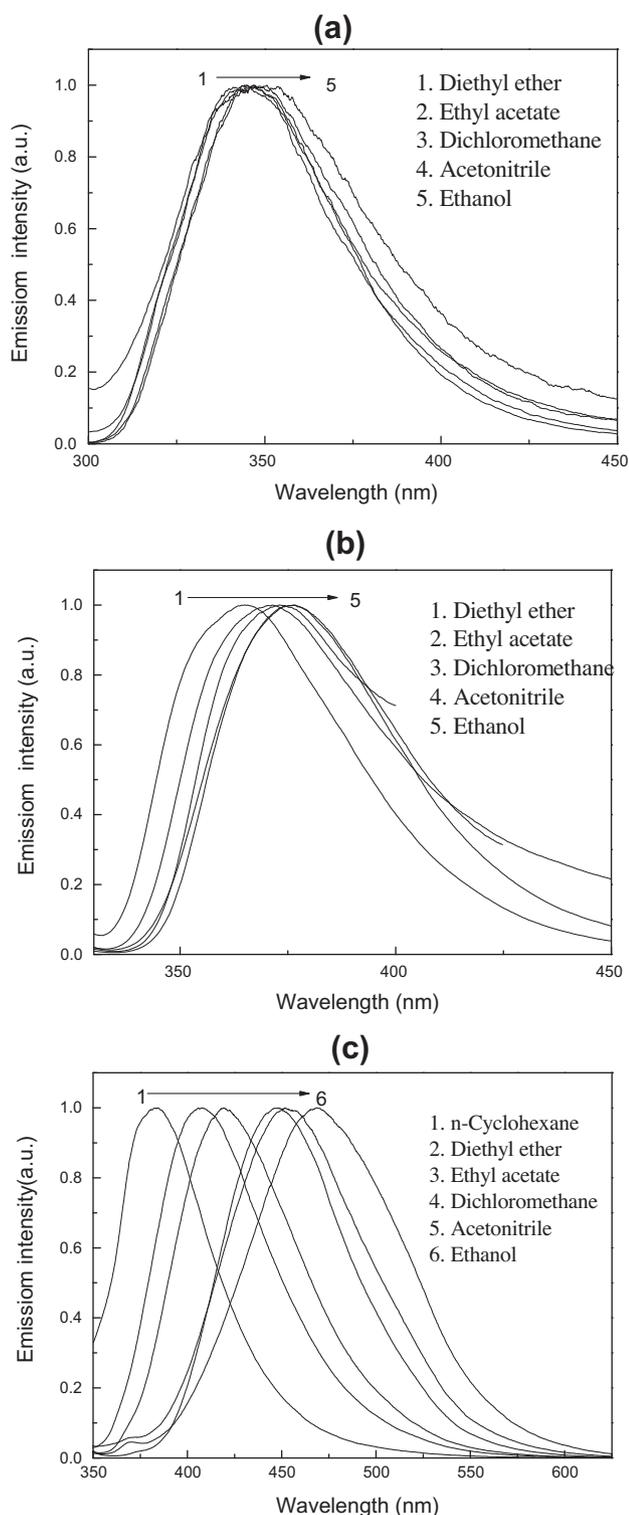
The absorption and fluorescence emission of compounds in various solvents.

Solvent	$\lambda_{\text{ab}}$ (nm)	$\lambda_{\text{em}}$ (nm)	$\lambda_{\text{em}1/2}$ (cm <sup>-1</sup> )	$\Delta\nu_{\text{stoke}}$ (cm <sup>-1</sup> )
<i>MMPAO</i>				
<i>n</i> -Hexane	272	-	-	-
Diethyl ether	271	-	-	-
Ethyl acetate	273	-	-	-
Dichloromethane	271	-	-	-
Acetonitrile	271	-	-	-
Ethanol	271	-	-	-
<i>MOPAO</i>				
<i>n</i> -Hexane	278	-	-	-
Diethyl ether	276	345	4486	7246
Ethyl acetate	279	347	4531	7024
Dichloromethane	277	351	4505	7611
Acetonitrile	278	347	4522	7153
Ethanol	277	354	4996	7953
<i>MDMAPAO</i>				
<i>n</i> -Hexane	315	-	-	-
Diethyl ether	316	368	3605	4473
Ethyl acetate	320	370	3880	4223
Dichloromethane	317	373	3736	4736
Acetonitrile	318	376	3619	4851
Ethanol	321	377	3640	4628
<i>MDPAPAO</i>				
<i>n</i> -Hexane	300, 324	385	3895	4890
Diethyl ether	310, 326	408	4064	6165
Ethyl acetate	300, 326	419	4136	6809
Dichloromethane	300, 328	448	3912	8167
Acetonitrile	301, 332	452	4176	7996
Ethanol	301, 333	468	4317	8662

- Not detected.

polarities. It was found that the absorption band has two peaks, the maximum absorption wavelength and the relative intensity of the longer absorption at around 330 nm was obvious dependence on the solvent polarity, whereas the shorter one at around 300 nm showed very weak dependence. The clearly observed dual absorption peaks could be readily assigned to the locally state and the ICT state, suggesting the ground state ICT interaction of MDPAPAO. By comparison, there is only one peak for MDMAPAO and the maximum absorption wavelength red-shifted slightly from *n*-cyclohexane to ethanol.

Table 1 lists the fluorescence emission peak maximum ( $\lambda_{\text{em}}$ ) of the oxazole compounds in different solvents. MMPAO does not show fluorescence in these organic solvents while the other oxazole compounds possess good fluorescence properties in the UV region as depicted in Fig. 2. These oxazole compounds display solvatochromic red-shift with increasing the solvent polarity. The shift is largest for MDPAPAO, smaller for MDMAPAO and smallest for MOPAO. The strong solvatochromic red-shift of MDPAPAO infers that it possesses an asymmetrically charge distributed state derived from the ICT of its fluorescent state. In addition, the emission bands display good normal Gaussian shape and their half



**Fig. 2.** Normalized fluorescence spectra of: (a) MOPAO, (b) MDMAPAO and (c) MDPAPAO in *n*-cyclohexane, diethyl ether, ethyl acetate, dichloromethane, acetonitrile, and ethanol. The concentrations are 0.5  $\mu\text{M}$ . The excitation wavelengths are 280, 315 and 325 nm, respectively.

bandwidths ( $\lambda_{\text{em}1/2}$ ) increases significantly with the increase in solvent polarity. The Stokes shift ( $\Delta\nu_{\text{stoke}}$ ) for MDPAPAO is very pronounced in polar solvents such as dichloromethane, acetonitrile and ethanol as displayed in Table 1. Again, all these data suggest that polar solvents could exhibit significant effect on the excited state of MDPAPAO.

Rettig and Zander state that ICT emission could be observed if the molecular system fulfill the conditions of Eqs. (2) and (3) [31,32]:

$$E_{\text{ICT}} - E_{\text{LE}} < 0 \quad (2)$$

$$E_{\text{ICT}} \approx IP_D - EA_A + E_{\text{Coul}} + E_{\text{solv}} \quad (3)$$

$E_{\text{ICT}}$  and  $E_{\text{LE}}$  are the energies of the lowest ICT state and the lowest locally excited state, respectively.  $IP_D$  and  $EA_A$  are the ionization potential and electron affinity potential of the donor and acceptor moieties, respectively.  $E_{\text{Coul}}$  is the Coulomb energy and  $E_{\text{solv}}$  is the interaction energy between the charge-separated molecule and the polar solvent. The  $EA_A$  is more or less the same for the oxazole compounds but the  $IP_D$  increases from MOPAO to MOPAO to MDMAPAO and then to MDPAPAO. It is well known that the red-shift in absorption spectrum of a compound depends on the electron-donating ability of its moiety; in other words, the larger the  $IP_D$ , the larger the red-shift of the absorption spectrum. For MDPAPAO, the triphenylamine moiety serves as an excellent electron donor when it links to the oxazole ring to form a D- $\pi$ -A structure; as a result, this provides a good basis for MDPAPAO to possess ICT character especially in the polar solvents. Further evidences including the changes in fluorescence emission spectrum, dipole moment and fluorescence lifetime with solvent polarity, and the interaction of MDPAPAO with  $\text{C}_{60}$  strongly support that MDPAPAO obviously possesses an ICT excited state. The details will be discussed in the subsequent sections.

#### Effect of solvent polarity on emission spectra and dipole moment

As the spectral characteristics of the oxazole compounds depend on the type of solvents, the effect of solvent polarity on their  $\lambda_{\text{em}}$  and Stokes shift are studied. Fig. 3 displays the plots of (a)  $1/\lambda_{\text{em}}$  against the solvent polarity parameter  $E_T(30)$  and (b) Stokes' shift against the polarity parameter  $f(\epsilon, n)$ . The plots of  $1/\lambda_{\text{em}}$  vs.  $E_T(30)$  are linear for the oxazole compounds, demonstrating that the solvent polarity is directly related to the emission peak of the oxazole compounds. In addition, the slope of the plot for MDPAPAO is steeper than that of MOPAO and MDMAPAO, indicating that the solvent polarity has more significant effect on MDPAPAO. These results suggest that the ICT state of MDPAPAO is more stable in polar solvents [33].

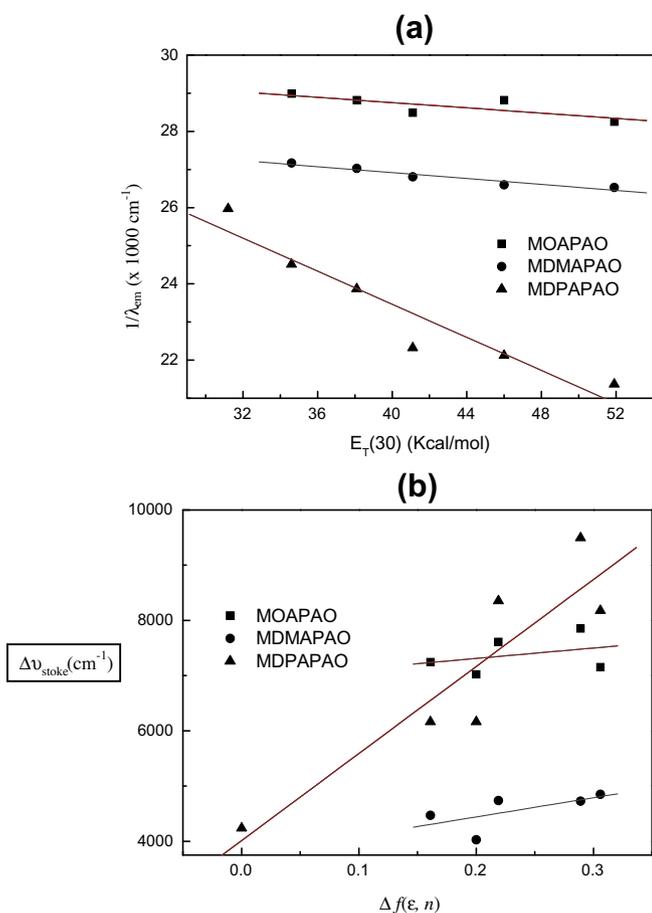
To determine the excited state dipole moment of the oxazole compounds, the Stokes shifts ( $\Delta\nu_{\text{stoke}}$ ) were plotted against the polarity parameter ( $\Delta f(\epsilon, n)$ ) as shown in Fig. 3b using the Lippert–Mataga Eqs. (4) and (5) [34]:

$$\nu_a - \nu_f = [2(\mu_e - \mu_g)^2 / 4\pi\epsilon_0 h c \rho^3] \Delta f(\epsilon, n) + \text{const} \quad (4)$$

$$\Delta f(\epsilon, n) = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1) \quad (5)$$

where  $\nu_a$  and  $\nu_f$  are the wavenumbers corresponding to the absorption and emission maxima of the compounds.  $\mu_e - \mu_g$  is the magnitude of the change in the dipole moment of the excited state and ground state,  $h$ ,  $c$ ,  $\epsilon_0$ ,  $\rho$  correspond to the Planck's constant ( $6.6 \times 10^{-34}$  J s), velocity of light in the vacuum ( $3.0 \times 10^8$   $\text{ms}^{-1}$ ), permittivity of vacuum ( $8.85 \times 10^{-12}$   $\text{V C}^{-1} \text{m}^{-1}$ ) and Onsager cavity radius (in meter), respectively. Using the assumption of Lippert, the Onsager cavity radius  $\rho$  can be derived from the length of the molecule multiplied by a reduction factor of 0.8 [35], giving the value 4.21, 4.32 and 4.57  $\text{\AA}$  for MOPAO, MDMAPAO and MDPAPAO, respectively.  $\epsilon$  and  $n$  are the dielectric constant and the refractive index of the solvent, respectively [36].

Fig. 3b displays that the plot of Stokes shift ( $\Delta\nu_{\text{stoke}}$ ) vs. ( $\Delta f(\epsilon, n)$ ) is linearly related. The change in dipole moment  $\mu_e - \mu_g$  for MOPAO, MDMAPAO and MDPAPAO were calculated as 3.9, 5.4 and 13.3,



**Fig. 3.** Effect of solvent polarity on the emission peak maxima and Stokes shift of MOPAO, MDMAPAO and MDPAPAO in *n*-cyclohexane, diethyl ether, ethyl acetate, dichloromethane, acetonitrile, and ethanol. Plots of: (a)  $1/\lambda_{em}$  ( $\times 1000 \text{ cm}^{-1}$ ) vs.  $E_T(30)$  and (b) Stokes shift ( $\times 1000 \text{ cm}^{-1}$ ) vs.  $f(\epsilon, n)$ .

respectively using the slopes of Eq. (4) and the Onsagar cavity radius  $p$ . The change in dipole moment for MDPAPAO was obviously larger than that of MOPAO and MDMAPAO. These results are in consistent with the solvent polarity dependence of the fluorescence spectra, possibly attributing to the stronger charge transfer effect from the electron rich donor to acceptor moieties in the excited state of MDPAPAO.

#### Fluorescence quantum yield

Table 2 summarizes the fluorescence quantum yields of MOPAO, MDMAPAO and MDPAPAO were determined in different solvents: diethyl ether, ethyl acetate, dichloromethane, acetonitrile and ethanol. The fluorescence quantum yields do not change significantly with the change of solvent polarity for the investigated compounds. The fluorescence quantum yields of MDPAPAO were found to be generally higher than that of MOPAO and MDMAPAO in all the solvents. A methyl carboxylate group is also present in

**Table 2**  
Fluorescence quantum yield of the oxazole compounds.

Solvent	MOPAO	MDMAPAO	MDPAPAO
Diethyl ether	0.019	0.016	0.886
Ethyl acetate	0.134	0.030	0.659
Dichloromethane	0.051	0.044	0.972
Acetonitrile	0.056	0.029	0.486
Ethanol	0.053	0.019	0.264

all these compounds and it is well known that many carbonyl compounds present a low-lying  $n-\pi^*$  state. The energy required for  $n-\pi^*$  and  $\pi-\pi^*$  electronic transitions are so close that  $n$  and  $\pi$  can form mixing states [37]. The high fluorescence quantum yield of MDPAPAO can be explained by a predominance of  $\pi-\pi^*$  character and  $n-\pi^*$  caused by the N atom and aryl in the triphenylamine moiety.

#### Fluorescent lifetime studies

The fluorescent decay of MOPAO, MDMAPAO and MDPAPAO were determined in different solvents (diethyl ether, ethyl acetate, dichloromethane, acetonitrile, and ethanol). Table 3 summarizes the lifetimes of these compounds in various solvents. It was found that MOPAO and MDMAPAO show a single exponential decay whereas MDPAPAO follows a bi-exponential fluorescence decay, inferring the existence of two different emissive states for MDPAPAO, i.e., the locally excited state (LE) and charge transfer state (ICT) [38]. The average lifetime ( $\tau$ ) is calculated and summarized in Table 3 using the following Eq. (6) [39]:

$$\tau = (a_1\tau_1^2 + a_2\tau_2^2)/(a_1\tau_1 + a_2\tau_2) \quad (6)$$

where  $\tau_1$  and  $\tau_2$  are the lifetime values of the two emissive states and  $a_1$  and  $a_2$  are called the pre-exponential factors, which give the abundance of each emissive state.

#### The inter-molecular charge transfer process of MDPAPAO with C<sub>60</sub>

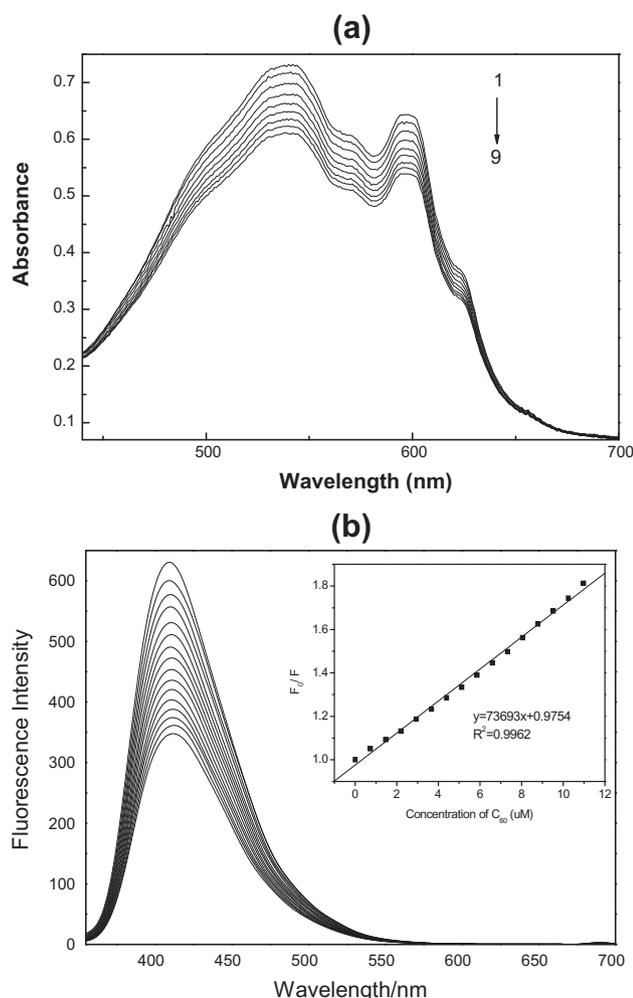
Among the wide variety of donor–acceptor systems, C<sub>60</sub> is particularly appealing as an electron acceptor because of its three-dimensional structure, delocalized  $\pi$ -electrons within the spherical carbon framework, small reorganization energy, low reduction potential, and absorption extending over most of the visible region. These unique physical and chemical properties make C<sub>60</sub> a promising candidate for investigating its electron transfer processes with electron-donor compounds [40–43]. Fig. 4a displays the UV–visible absorption spectrum of C<sub>60</sub> in the presence of various concentrations of MDPAPAO. C<sub>60</sub> has a strong absorption band at about 450–650 nm in the visible light region, deriving from the symmetry-forbidden electronic transitions and the symmetry-allowed vibronic transitions [44,45]. Since MDPAPAO does not absorb at wavelengths longer than  $\sim 450$  nm, the C<sub>60</sub> absorption band at 450–650 nm was chosen to investigate the CT interaction between MDPAPAO and C<sub>60</sub>. The absorption intensity of C<sub>60</sub> decreases with the increase in concentration of MDPAPAO, attributing to the formation of inter-molecular CT complex [32]. By contrast, there is almost no change in spectral characteristic and absorption intensity of C<sub>60</sub> in the presence of the other three oxazole compounds (MMPAO, MOPAO and MDMAPAO), inferring that they have weak or no interaction with C<sub>60</sub>.

Fig. 4b depicts the fluorescence quenching of C<sub>60</sub> on MDPAPAO. The maximum excitation wavelength is 330 nm, but C<sub>60</sub> have

**Table 3**  
The fluorescence lifetime of oxazole compounds.

Solvent	MOPAO	MDMAPAO	MDPAPAO		
	$\tau$ (ns)	$\tau$ (ns)	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau$ (ns)
Diethyl ether	1.79	1.64	1.90	3.91	3.20
Ethyl acetate	4.53	1.87	4.00	8.17	4.55
Dichloromethane	1.70	3.68	6.12	7.97	7.23
Acetonitrile	3.92	1.91	4.61	7.25	5.61
Ethanol	2.31	1.66	3.72	7.15	3.72

$\tau_1$ ,  $\tau_2$  are the fluorescence decay of the locally excited state (LE) and the charge transfer state (ICT), respectively [29,38].  $\tau$  is the average lifetime of MDPAPAO in the fourth column [39].



**Fig. 4.** (a) UV–visible absorption spectrum of 0.275 mM  $C_{60}$  in toluene in the presence of various concentrations of MDPAPAO: (1) 0.0, (2) 0.0366, (3) 0.0644, (4) 0.0936, (5) 0.121, (6) 0.147, (7) 0.172, (8) 0.195, and (9) 0.217 mM. (b) Fluorescence quenching effect of  $C_{60}$  on the emission spectrum of 0.235 mM MDPAPAO in toluene. The concentrations of  $C_{60}$  are (1) 0.0, (2) 1.83, (3) 3.68, (4) 5.49, (5) 7.33, (6) 9.16, (7) 11.0, (8) 12.8, (9) 14.7, (10) 16.5, (11) 18.3, (12) 20.2, (13) 22.0, (14) 23.8, (15) 25.6 and (16) 27.5  $\mu\text{M}$ . The inset displays the Stern–Volmer plot of  $C_{60}$ , where  $F_0$  and  $F$  are the emission intensities of MDPAPAO in the absence and presence of  $C_{60}$ . The excitation wavelength is 345 nm.

strong absorption bands at about  $\sim 290$  and  $\sim 320$  nm with tail extending to 340 nm, so the excitation wavelength at 345 nm was chosen to study the interaction between MDPAPAO and  $C_{60}$ . From the Fig. 4b we can find that the emission intensity decreases with the increase in concentration of  $C_{60}$ . It is obvious that the emission of MDPAPAO is seriously quenched by  $C_{60}$ . The inset displays the Stern–Volmer plot ( $F_0/F = 1 + K_{SV}[C_{60}]$ ,  $K_{SV} = k_q\tau$ ) of  $C_{60}$ , where the  $F_0$  and  $F$  are the emission intensity of MDPAPAO in the absence and presence of  $C_{60}$ , and  $K_{SV}$  is the Stern–Volmer constant. A linear straight line is obtained. The fluorescence lifetime of MDPAPAO was 3.51 ns in toluene, the quenching rate constant  $k_q$  was  $2.1 \times 10^{13}$  L/(mol s). The fluorescence emission extending to 600–700 nm was measured and the  $C_{60}$  fluorescence was not appeared in the 600–700 region, indicating that  $C_{60}$  can efficiently quench the photo-induced ICT process of the triphenylamine system in MDPAPAO with  $C_{60}$  acting as the electron acceptor [46].

## Conclusion

New 2-phenyloxazoles MMPAO, MOPAO, MDMAPAO, and MDPAPAO have been successfully synthesized and their photo-

physical properties were investigated in detail. The results show that MMPAO, MOPAO and MDMAPAO have lower fluorescence quantum yields. Their quantum yield, fluorescence lifetime and spectral characteristics are less dependent on the solvent polarity. By contrast, MDPAPAO displays larger changes in fluorescence emission spectrum, dipole moment and quantum yield in different solvent polarity. The bi-exponential fluorescence decay behavior of MDPAPAO indicates that the triphenylamine moiety on MDPAPAO can enhance its ICT character as well as increase its fluorescence quantum yield. In addition,  $C_{60}$  could efficiently quench the fluorescence emission of MDPAPAO, inferring that  $C_{60}$  can inhibit the ICT of MDPAPAO. The special ICT properties of MDPAPAO could possibly facilitate its use as a laser dye, fluorescent probe and luminescent material in the many fields.

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