

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



journal homepage: www.elsevier.com/locate/saa

UV-vis spectroscopy and semiempirical quantum chemical studies on methyl derivatives of annulated analogues of azafluoranthene and azulene dyes

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ARTICLE INFO

Article history: Received 20 January 2010 Received in revised form 16 March 2010 Accepted 8 April 2010

Optical absorption spectra Fluorescence spectra Semiempirical calculations Organic dyes

ABSTRACT

Paper reports the measured optical absorption and fluorescence spectra of 4-(2-chlorophenyl)-7-methyl-1,3-diphenyl-1H-pyrazolo[3,4-b]quinoline (MCPDPPQ), as well as 6-methyl-1,3-diphenyl-3H-indeno (MDPIPO) [1,2,3-*de*]pyrazolo[3,4-*b*]quinoline and 9-methyl-6-phenyl-6H-5,6,7-triazadibenzo [f,h]naphtho[3,2,1-cd]azulene (MPTNA) representing cyclized five- or seven-membered regioisomeric products of MCPDPPQ, respectively. The spectra has been recorded in solvents of different polarity and compared with the results of quantum chemical calculations performed by means of the semiempirical method PM3 in combination with molecular dynamics (MD) simulations. Cyclization of MCPDPPQ into MDPIPQ or MPTNA is accompanied by a significant red shift of the first optical absorption and fluorescence bands. While the solvent polarity rises all the dyes exhibit the blue shift of the first absorption band and the red shift of the fluorescence band. These trends have been reproduced within the semiempirical calculations in combination with the Lippert-Mataga dielectric polarization model and explained by specific orientations of the dipole moments in the ground and excited states. All dyes may be considered as candidates for the luminescent or electroluminescent applications. Depending on solvent polarity they emit light in the green-yellow range of the visible spectra.

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1. Introduction

In the past decade much attention has been focused on the spectral properties of numerous low weight organic dyes in a context of their broad range of applications in optoelectronics, mainly as fluorescence dopants for dye lasers [1-3] or electroluminescent devices such as organic light emitting diodes or electroluminescent displays [4-6]. Synthesis of new molecules with desirable fluorescence properties has always been a challenging and difficult task. In our group we have been dealing for many years with pyrazoloquinoline (PQ) dyes [7-21] being good candidates for blue or blue-green fluorescence emitters in polymer layer host. Being inspired by an interesting heptacyclic arene of rubicene [22], we decided to start a new program focused on the synthesis of annulated analogues of azafluoranthenes and heteroazulenes. starting from the derivatives of PO [23]. During our preliminary studies we observed the possibility from the same starters, i.e. 4-(2-chlorophenyl)-7-methyl-1,3-diphenyl-1H-pyrazolo[3,4-b] quinoline (hereafter MCPDPPQ) or 4-(2-bromophenyl)-7-methyl1,3-diphenyl-1*H*-pyrazolo[3,4-b]quinoline (hereafter MBPDPPQ), to synthesize the two regioisomers: 6-methyl-1,3-diphenyl-3*H*-indeno[1,2,3-*de*]pyrazolo[3,4-*b*]quinoline (MDPIPQ) and 9-methyl-6-phenyl-6*H*-5,6,7-triazadibenzo[*f*,*h*]naphtho[3,2,1-*cd*] azulene (MPTNA). The chemical structures of MCPDPPQ (MBPDPPQ), MDPIPQ and MPTNA dyes may be presented by the following scheme



where depending on chemical reaction conditions, as described in Ref. [23], one obtains from MCPDPPQ either MDPIPQ or MPTNA molecule. Especially interesting is isomer MPTNA because of its novelty including an additional fused seven-membered ring. Similar arrangements of atoms can be exemplified in the structures of acepleiadylene [24], triazadibenzo[*cd*, *g*]azulenes [25], and in carbon nanotubes as so-called Stone-Wales defects

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giving rise to different deformations of carbon nanotubes [26].

In the present paper we report the optical absorption and fluorescence spectra of the starter compound MCPDPPQ as well as its regioisomeric products, i.e. five-membered MDPIPQ or sevenmembered MPTNA cyclized molecular conformations. The aim behind of these investigations is to study an influence of the two types of the cyclizations on the electronic properties of the regioisomers representing annulated analogues of azafluoranthene and azulene dyes. On the other hand, we analyze also the change of the electronic structure caused by solvent-modified electron transfer interactions. For this reason the optical absorption and photoluminescence spectra of starter compound MCPDPPQ and its regioisomeric products MDPIPQ or MPTNA are recorded in organic solvents of different polarity and consequently subjected to quantum chemical analysis within the semiempirical model PM3.

2. Synthesis

General routines concerning the synthesis of heterocycles dyes are presented in Ref. [23]. Commercially available reagents (Aldrich, Fluka, Merck) were used without further purification. ¹H NMR and ¹³C NMR were recorded using a Mercury-Vx 300MHz Varian operating at 300 MHz respectively in CDCl₃ with tetramethylsilane (TMS) as an internal standard. Melting points were measured on a MELT-Temp and are uncorrected. The purity of the obtained compounds was checked by TLC. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

Heating *m*-anisidine, pyrazolone and 2-halobenzaldehyde in boiling ethylene glycol produced exclusively **2**, which is consistent with our previous findings [23], see scheme below.

products. Thereby using bromine derivative is found to be more preferable.

2.1. 4-(2-Chlorophenyl)-7-methyl-1,3-diphenyl-1H-pyrazolo [3,4-b]quinoline (**2a**, MCPDPPQ)

Yellow solid; $R_f = 0.57$; Mp = 194–196 °C; H¹ NMR (CDCl₃, 300 MHz) δ 2.60 (s, 3H, Me), 7.06–7.34 (m, 11H), 7.52 (d, 1H, J = 9.0 Hz), 7.57 (t, 2H, J = 7.5 Hz), 8.05 (s, 1H), 8.61 (d, 2H, J = 8.7 Hz); Anal. Calcd. for C₂₉H₂₀ClN₃; C, 78.11; H, 4.52; N, 9.42. Found: C, 78.01; H, 4.88; N, 9.26.

2.2. 4-(2-Bromophenyl)-7-methyl-1,3-diphenyl-1H-pyrazolo [3,4-b]quinoline (**2b**, MBPDPPQ)

Yellow solid; $R_f = 0.57$; Mp = 208–211 °C; H¹ NMR (CDCl₃, 300 MHz) δ 2.59 (s, 3H, Me), 7.06–7.25 (m, 9H), 7.31 (t, 1H, J = 7.5 Hz), 7.50–7.55 (m, 2H), 7.57 (t, 2H, J = 7.5 Hz), 8.05 (s, 1H), 8.62 (d, 2H, J = 8.7 Hz); Anal. Calcd. for C₂₉H₂₀BrN₃; C, 71.03; H, 4.11; N, 8.57. Found: C, 71.14; H, 4.34; N, 8.61.

2.3. 9-Methyl-6-phenyl-6H-5,6,7-triazadibenzo[f,h]naphtho [3,2,1-cd]azulene (**3**, MPTNA)

Yellow solid; $R_f = 0.63$; Mp = 272–273 °C; H¹ NMR (CDCl₃, 300 MHz) δ 2.57 (s, 3H, Me), 7.24 (d, 1H, J = 1.5 Hz), 7.29 (t, 1H, J = 7.5 Hz), 7.37–7.52 (m, 4H), 7.56 (t, 2H, J = 7.5 Hz), 7.73 (dd, 1H, J = 7.8, 1.5 Hz), 7.79–7.83 (m, 1H), 7.85 (dd, 1H, J = 7.8, 1.5 Hz), 7.79–7.83 (m, 1H), 7.85 (dd, 1H, J = 7.8, 1.5 Hz), 7.94 (s, 1H), 8.31–8.34 (m, 2H), 8.60 (d, 2H, J = 8.7 Hz); Anal. Calcd. for C₂₉H₁₉N₃; C, 85.06; H, 4.68; N, 10.26. Found: C, 84.90; H, 4.76; N, 10.01.



The rationale to place the methyl group at 7-position of **2** is to exclude any steric obstacle close to the site of cyclization in case of formation of **4**. The seven-membered **3** analogue can be prepared from both haloderivatives **2a,b**, but **4** is best obtained from **2b** using a palladium catalyst [23,27]. Treating chlorine analogue **2a**, as described either by Jackson et al. [28] or Smet et al. [29], did not give quite satisfactorily results, because most of a starting material indeed was not converted into final

2.4. 6-Methyl-1,3-diphenyl-3H-indeno[1,2,3-de]pyrazolo [3,4-b]quinoline (**4**, MDPIPQ)

Orange solid; $R_f = 0.46$; Mp = 224–226 °C; H¹ NMR (CDCl₃, 300 MHz) δ 2.64 (s, 3H, Me), 6.92 (dq, 1H, J = 7.8, 0.6 Hz), 7.04 (td, 1H, J = 8.7, 1.2 Hz), 7.33 (t, 2H, J = 7.2 Hz), 7.54–7.63 (m,

6H), 7.76–7.84 (m, 4H), 8.54 (d, 2H, J = 8.7 Hz); Anal. Calcd. for C₂₉H₁₉N₃; C, 85.06; H, 4.68; N, 10.26. Found: C, 85.09; H, 4.90; N, 10.36.

3. Experimental and calculation procedures

To probe the solvatochromic effect on the optical absorption and fluorescence spectra the measurements have been carried out using as solvents cyclohexane (CHX), tetrahydrofuran (THF) and acetonitrile (ACN). The molar concentration of the dyes subjected to investigations was about 10⁻⁵ M in each case. The measurements were performed by means of Shimadzu UV-VIS 2101 scanning spectrophotometer in the range of 230-600 nm using a standard 1 cm path length quartz cuvette for absorption spectrometry. The steady-state fluorescence spectra have been excited by a mercury lamp ($\lambda_{ex} = 365 \text{ nm}$) and recorded in a single photon counting mode. Accordingly, the setup consisted of a conventional spectrofluorimeter equipped by the cooled photomultiplier EMI 955 8B. The fluorescence spectra were corrected for the spectral sensitivity of the detecting system. The samples (prepared in the darkness) were degassed before experiments using the freezing-pumping-thawing technique. The fluorescence quantum yields were determined from the steady-state measurements using the solution of quinine sulphate in 0.05 M H₂SO₄ as an actinometer ($\Phi_{fl} = 0.53$). The lifetimes were determined in the time-resolved single photon counting regime by analyzing the temporal decay of the fluorescence spectra being excited by picosecond diode laser (IBH-UK, $\lambda = 400$ nm, $\tau = 70$ ps pulse duration).

The quantum chemical analysis has been performed by means of the software package HyperChem-8.0 within the semiempirical method PM3 (Parametric Model 3). The geometrical optimization in the ground state and the molecular dynamics (MD) simulations has been performed using the same Hamiltonian, PM3. The transition dipole moments $[\vec{\mu}_{0i} \equiv \vec{\mu}(S_0 \rightarrow S_i)]$ and the excitation energies $[\Delta E_{0i} = E(S_i) - E(S_0)]$ between the ground state (S_0) and the excited states $(S_i, i \ge 1)$, representing the configuration interaction (CI) singlet states, as well as the state dipole moments $[\vec{\mu}_i \equiv \vec{\mu}(S_i)]$ were calculated taking into account only the singly excited CI limited by a set of 16 occupied and 16 unoccupied orbitals. Such calculation procedure has been applied either to a certain equilibrium molecular conformation (EMC) in vacuo (T = 0 K) or combined with the MD simulations at T = 300 K. In the second case we consider a molecular dynamic trajectory generated within the standard MD procedure at a certain simulation temperature and consisting of about 200 consequent instantaneous conformations that were subjected to further quantum chemical calculations. The optical absorption spectra in this case is just an average over all the consequent conformations. For each particular conformation of such MD trajectory the band shape of simulated optical absorption spectra is assumed to be defined by the Gaussian function, i.e. \propto $v_{0i}|\vec{\mu}_{0i}|^2 \exp\{-2.773[(h\nu - \Delta E_{0i})/\Gamma]^2\}$, where $v_{0i} = \Delta E_{0i}/h$, h is the Planck constant, Γ is the empirical model parameter describing the Gaussian lineshape broadening. It has been adjusted in each case in order to reproduce experimental bandwidth of measured absorption bands. The total time of the simulated MD trajectories has been chosen for all dyes as 50 ps. It is certainly much longer compared to a vibration/rotation temporal periods of the slowest molecular moieties like methyl (Me) or phenyl (Ph) groups. Accordingly, the resulting spectra usually well converged already after the calculations of 100-150 conformations. For this reason the length of the MD trajectory, consisted of 200 conformations, should be sufficient in order to satisfy the convergence criteria.



Fig. 1. The equilibrium molecular conformations of MCPDPPQ, MDPIPQ and MPTNA dyes as obtained within the semiempirical quantum chemical method PM3. ϕ_1 , ϕ_2 or ϕ_0 are the torsion angles defining the angular orientation of the phenyl rings Ph1, Ph2 or Ph0, respectively.

4. Results and discussion

The geometry optimization of MCPDPPQ, MDPIPQ and MPTNA dyes, performed within the semiempirical method PM3, leads to the equilibrium conformations as shown in Fig. 1. Each of the dyes are characterized by several equilibrium molecular geometries with nearly the same total energy. Such equilibrium states differ each other mainly by angular orientations of their phenyl rings Ph0, Ph1 or Ph2 which are defined in our case by the torsion angles ϕ_0 , ϕ_1 or ϕ_2 , respectively (see Fig. 1). Fig. 2(a)–(e) shows



Fig. 2. The angular diagrams of the ground state energy $E(\phi)$ as calculated in the GP (E_{GP} , blue color) and ACN solution (E_{ACN} , red color) and corresponding to it population distribution $p(\phi)$ in the GP (gray color) and ACN solution (black color). Blue dashed lines in sections (b) and (d) correspond to metastable states. (a) $E(\phi_1)$ and $p(\phi_1)$ for Ph1 unit of MCPDPPQ dye. (b) $E(\phi_2)$ and $p(\phi_2)$ for Ph2 unit of MCPDPPQ dye. (c) $E(\phi_1)$ and $p(\phi_1)$ for Ph1 unit of MDPIPQ dye. (d) $E(\phi_2)$ and $p(\phi_2)$ for Ph2 unit of MDPIPQ dye. (e) $E(\phi_0)$ and $p(\phi_0)$ for Ph0 unit of MPTNA dye. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

the total molecular energy *E* vs the torsion angle ϕ ($\phi = \phi_0, \phi_1$ or ϕ_2) that have been calculated for the restrained geometries, i.e. the conformations being obtained within a forced optimization procedure for a sequence of fixed angular orientations of a particular phenyl group. The blue and red lines correspond here to the energy E_{GP} in the gas phase (GP) and ACN solution (E_{ACN}), respectively. In the GP the chlorophenyl unit of MCPDPPQ is oriented almost orthogonally (torsion angle $\phi \approx 91^\circ$) whereas the two other phenyl rings, Ph1 and Ph2, being linked to PQ group by C-C and C-N bonds, respectively, are characterized by the equilibrium torsion angles $\phi_{1eq} \approx 112 \ (\pm n \cdot 180, \ n = 0, 1, 2, \ldots)$ deg and $\phi_{2eq} \approx 19$ or -19 $(\pm n \cdot 180, n = 0, 1, 2, ...)$ deg. In addition, the $E_{GP}(\phi_2)$ -dependence (Fig. 2(b)) indicates also on the two metastable conformational states at $\phi_2 \approx \pm 42 (\pm n \cdot 180, n = 0, 1, 2, ...)$ deg and is almost symmetric with respect to the angle of 90 ($\pm n \cdot$ 90, n = 0, 1, 2, ...) deg. Contrary to this, due to a presence of the Cl atom, the Ph1 group appears in substantially asymmetric double-well potential as one may see in Fig. 2(a). Similarly, MPTNA (see Fig. 2(e)) is also characterized by essentially asymmetric potential in regards to its PhO moiety and exhibits the equilibrium twist angles ϕ_{0eq} at about -17° and 45°, respectively. Such asymmetry is obviously related with a specific geometry of phenyl-azulene moiety of MPTNA having substantially bent shape in the ground state (see Fig. 1). On the other hand, the phenyl-azafluoranthene moiety of MDPIPQ is perfectly flat. Accordingly, the orientation of Ph2 ring in the GP corresponds to a symmetric potential (see Fig. 2(d)) with the equilibrium torsion angles $\phi_{2eq} \approx \pm 23 \ (\pm n \cdot 180, n = 0, 1, 2, ...)$ deg, representing two stable energy equivalent conformations, and the two metastable conformations with $\phi_2 \approx \pm 46 \ (\pm n \cdot 180, n = 0, 1, 2, ...)$ deg. The Ph1 ring of MDPIPQ in the GP is characterized by nearly twisted equilibrium angular position ($\phi_{1eq} \approx 90 \ (\pm n \cdot 180, n = 0, 1, 2, ...)$ deg, see Fig. 2(c)), however due to a very flat shape of $E(\phi_1)$ in the vicinity of $\phi_{1eq} = 90^\circ$ its exact angular position may be defined with a relatively low precision, i.e. $\Delta \phi_1 = \pm 3^\circ$. In the polar solvents the equilibrium torsion angles are subjected to their modifications. To have an idea how the solvation influences them the total molecular energy in ACN solution $E_{ACN}(\phi)$ was evaluated from the angular dependences of the ground state energy $E_{CP}(\phi)$ and dipole moments $\mu_g(\phi)$ (calculated in the GP) and the Onsager cavity radius a_0 [30] (taken as 4.4 Å for all dyes) using the following equation [31,32]:

$$E_{ACN}(\phi) = E_{GP}(\phi) - \frac{\mu_g^2(\phi)}{a_0^3} \frac{\varepsilon - 1}{2\varepsilon + 1}$$
(1)

where $\varepsilon = 37.5$ is the static dielectric constant of ACN. From Fig. 2(a)–(e) one can realize that in ACN environment the Ph1 ring of both MCPDPPQ and MDPIPQ tends to a more twisted orientations whereas Ph2 unit of these molecules as well as the Ph group of MPTNA tend to more planar ones. However, the changes in angular orientations of aromatic groups are rather moderate for all dyes and do not exceeds few degrees. On the other hand, in all the cases the



Fig. 3. The optical absorption spectra of MCPDPPQ (black color), MDPIPQ (red color) and MPTNA (blue color) dyes as measured (a) and calculated (b) within the semiempirical quantum chemical method PM3. Vertical lines in section (b) are the calculated optical absorption spectra of equilibrium molecular conformations (EMC) ($\Gamma = 0 \text{ eV}$), solid curves are the optical absorption spectra being calculated within the MD simulations at T = 300 K and Gaussian lineshape broadening ($\Gamma = 0.24 \text{ eV}$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

energy barriers between the equilibrium angular orientations of the phenyl rings are of the order of k_BT (k_B is the Boltzmann constant) or less this magnitude thus according to the Boltzmann statistic one may expect rather large angular amplitudes in their rotational dynamics at room temperature (T = 300 K). Our further quantitative evaluations are based therefore on the population analysis both in the GP and ACN solution. Following to it the population distribution $p(\phi)$, being presented in Fig. 2(a)–(e), has been evaluated as $p(\phi) = p_0 \exp(-E(\phi)/k_BT)$, where $p_0 = \left[\int_0^{2\pi} \exp(-E(\phi)/k_BT)\right]^{-1}$ is the normalization factor and $E \equiv E_{GP}$ or E_{ACN} . One can see that even for the Ph1 group of MCPDPPQ and MDPIPQ its angular deviation may be rather large, roughly up to 40° for MDPIPO and about up to 45° for MCPDPPQ. The situation with the Ph2 ring of these dyes as well as the PhO group of MPTNA is even more dramatic since the population *p* is considerable here over the complete angular range. For this reason the molecular dynamics aspects of MCPDPPQ, MDPIPQ and MPTNA dyes appear in the focus of our studies and will be considered in further analysis of their spectroscopic properties.

Fig. 3(a) shows the optical absorption spectra of the MCPDPPQ, MPTNA and MDPIPQ measured in weakly polar CHX solvent. In the range of 230–600 nm the absorption spectrum of these dyes are characterized by several broad absorption bands with the most strongest ones in the region of 250–300 nm. MCPDPPQ exhibits the first absorption band being unstructured and centered at about 398 nm. Cyclization of MCPDPPQ into MPTNA or MDPIPQ leads to its significant red shift. For MPTNA or MDPIPQ dyes the first absorption band looks almost unstructured and exhibits nearly the same



Fig. 4. Solvatochromism of MCPDPPQ, MDPIPQ and MPTNA dyes. Sections (a), (c) and (e) show the optical absorption spectra in the region of the first absorption band measured in CHX (blue) and ACN (red) solutions. Sections (b), (d) and (f) are the calculated optical absorption spectra in the GP (blue) and ACN solution (red), respectively. Here the vertical lines are the spectra calculated by PM3 method for equilibrium molecular conformations (EMC) ($\Gamma = 0 \text{ eV}$) and the solid curves are the spectra being calculated within PM3 method in combination with the MD simulations at T = 300 K and Gaussian lineshape broadening ($\Gamma = 0.24$ eV). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

spectral positions at about 449 nm. Semiempirical quantum chemical analysis quite properly describes such trend for both dyes, see Fig. 3(b). However the magnitudes of corresponding spectral shifts appears to be somewhat smaller comparing to the obtained experimental value $\Delta\lambda(exp) \approx 51$ nm. In particular, the calculations for equilibrium conformations in the GP (T = 0 K, $\Gamma = 0$) give $\Delta\lambda(EMC) \approx 28$ nm whereas the spectra obtained within the MD simulations (T = 300 K, $\Gamma = 0.24$ eV) reveal a bit larger spectral shift, i.e. $\Delta\lambda(MD) \approx 31$ nm.

While the solvent polarity changes from CHX to ACN the spectral position of the first absorption band of MCPDPPQ, MDPIPQ and MPTNA dyes exhibits a blue shift of about 6–8 nm, see Fig. 4(a), (c) and (e), respectively. Such hypsochromic shift in the optical absorption is accompanied by a bathochromic (red) shift of the fluorescence spectra (Fig. 5). MCPDPPQ and especially MDPIPQ reveal relatively stronger solvatochromism of their fluorescence bands comparing to MPTNA dye for which the red shift of the fluores-



Fig. 5. Steady-state normalized fluorescence spectra of MCPDPPQ (a), MDPIPQ (b) and MPTNA (c) dyes being measured in CHX (blue) and ACN (red) solutions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

cence is of several time weaker. In the highly and medium polar solvents the photoluminescence spectra are unstructured. However, some vibronic structuring of the photoluminescence bands occurs in weakly polar CHX being more evidently seen for MDPIPQ and MPTNA dyes (see Fig. 5(b) and (c)).

The absorption and emission maxima of MPTNA and MDPIPQ obtained in solvents of different polarity are reported in Table 1 together with the measured quantum yield Φ_{fl} and the fluorescence lifetime τ_{fl} . The radiationless (k_{nr}) and radiative (k_{fl}) rate constants as well as the fluorescence transition moment M_{fl} have been evaluated within a simple kinetic model of an irreversible excited charge transfer state formation as in Ref. [33]:

$$k_{nr} = \frac{1 - \Phi_{fl}}{\tau_{fl}}, \qquad k_{fl} = \frac{\Phi_{fl}}{\tau_{fl}}$$
(2)

$$|M_{fl}|^2 = \frac{3hk_{fl}}{64\pi^4 n^3 v_{fl}^3}$$
(3)

The photophysical constants of MCPDPPQ, MPTNA and MDPIPQ dyes in different solutions.

Table 1

where $v_{fl} = 1/\lambda_m^{fl}$, *n* is the solvent refractive index. All the dyes exhibit rather similar values of M_{fl} in different solvents. While the solvent polarity changes from CHX to ACN the fluorescence moment of MCPDPPQ, MPTNA or MDPIPQ dyes decreases accordingly on about of 11, 6 or 15% only. This fact suggests that the electronic structure and molecular conformation of the fluorescent states should not change significantly with the solvent polarity.

In a simple approximation the solvatochromic shift can be evaluated within the Lippert–Mataga dielectric polarization model [13,14]. In accordance to this approach the solvent-modified wavenumbers of the optical absorption ($\nu^{abs} = 1/\lambda^{abs}$) or fluorescence ($\nu^{fl} = 1/\lambda^{fl}$) maxima are defined as [34,35]:

$$v^{abs} = v_0^{abs} - \frac{2\vec{\mu}_g(\vec{\mu}_e - \vec{\mu}_g)F(\varepsilon, n)}{hca_0^3}$$
(4)

$$\nu^{fl} = \nu_0^{fl} - \frac{2\vec{\mu}_e(\vec{\mu}_e - \vec{\mu}_g)F(\varepsilon, n)}{hca_0^3}$$
(5)

where

$$F(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{1}{2} \frac{n^2 - 1}{2n^2 + 1}$$

$$\tag{6}$$

is the solvent polarity function; v_0^{abs} and v_0^{fl} are the spectral positions of the absorption and fluorescence maxima in the GP, correspondingly; *c* is the light speed in vacuo; *n* is the refractive index of the solvent, ε is the static dielectric constant of the solvent, $\vec{\mu}_{g}$ and $\vec{\mu}_e$ are the ground and the excited state dipole moments, respectively. Fig. 4(b), (d) and (f) show the first optical absorbtion band of MCPDPPQ, MDPIPQ and MPTNA dyes, respectively, being calculated by PM3 method in the GP (F = 0) as well as in ACN solution (F = 0.393) using the solvatochromic correction as defined by Eq. (4). One can see, that the semiempirical calculations in combination with the dielectric polarization model, applied to EMC, describes properly the hypsochromic trend in the solvatochromic behavior of the first optical absorbtion band (see vertical lines in Fig. 4(b), (d) and (f)). Moreover, with the Onsager cavity radius $a_0 = 4.4$ Å they give as well a reasonable value as for the shift itself. Also importantly, the solvatochromic shift keeps the same trends and exhibits similar magnitudes in the MD simulations (see continuous curves in Fig. 4(b), (d) and (f)). This finding means that a rotational dynamics of phenyl rings, being characterized by guite strong angular amplitudes in all the dyes at T = 300 K, indeed does not influences the hypsochromic trend and only slightly modifies its magnitude. Fig. 6 shows the wavenumbers v_m^{abs} and v_m^{fl} vs the solvent polarity

Fig. 6 shows the wavenumbers ν_m^{abs} and ν_m^{l} vs the solvent polarity *F* being extracted from the measured optical absorbtion and fluorescence spectra. The slopes of the linear plots allow to determine directly the values of $\vec{\mu}_g(\vec{\mu}_e - \vec{\mu}_g)/a_0^3$ and $\vec{\mu}_e(\vec{\mu}_e - \vec{\mu}_g)/a_0^3$ which are collected in Table 2. On the other hand, they can be evaluated having the ground and excited state dipole moments being calculated within the semiempirical model PM3. Importantly, that the quantum chemical calculations give for both dyes a proper

Compound	Solvent	λ_m^{abs} (nm)	λ_m^{fl} (nm)	Φ_{fl}	τ_{fl} (ns)	$k_{nr} (\times 10^7, s^{-1})$	$k_{fl} (\times 10^7,{ m s}^{-1})$	M_{fl} (D)
MCPDPPQ	CHX	398	452	0.8	17.2	1.2	4.7	2.17
MDDIDO	CUX	440	402	0.07	11.0	1.5	2.5	1.55
MIDPIPQ	THF	449	546	0.37	12.4	5.5 6.5	1.5	1.70
	ACN	441	562	0.103	7.4	1.2	1.4	1.80
MPTNA	CHX	450	524	0.49	16.6	3.1	3.0	2.16
	THF ACN	448 444	536 540	0.365 0.34	16.9 17.2	3.8 3.8	2.2 2.0	1.96 2.02

 λ_m^{abs} is the absorption maxima, λ_m^{fl} is the fluorescence maxima, Φ_{fl} is the fluorescence quantum yield, τ_{fl} is the fluorescence lifetime, k_{nr} is the radiationless rate constant, k_{fl} is the radiative rate constant and M_{fl} is the fluorescence moment.



Fig. 6. The solvatochromic shift of the optical absorption $[\nu_m^{abs} = (\lambda_m^{abs})^{-1}]$ and fluorescence $[\nu_m^{fl} = (\lambda_m^{fl})^{-1}]$ maxima vs solvent polarity *F*.

Table 2

Slopes of the solvatochromic plots for MCPDPPQ, MDPIPQ and MPTNA dyes as determined from optical absorption and fluorescence measurements and calculated within the semiempirical model PM3.

Compound	$ec{\mu}_g(ec{\mu}_e-ec{\mu}_g)/a_o^3~(ext{eV})$	$ec{\mu}_e(ec{\mu}_e-ec{\mu}_g)/a_o^3~(\mathrm{eV})$				
MCPDPPQ						
Exp.	-0.076	0.293				
Calc.(MD)	-0.085	-				
Calc.(EMC)	-0.066	0.006				
MDPIPQ						
Exp.	-0.086	0.377				
Calc.(MD)	-0.113	-				
Calc.(EMC)	-0.078	0.044				
MPTNA						
Exp.	-0.064	0.12				
Calc.(MD)	-0.102	-				
Calc.(EMC)	-0.079	0.04				

signs for the slopes regarding the solvatochromic behavior and explain why the bathochromic (red) shift of the fluorescence band is accompanied by the hypsochromic (blue) shift of the absorption band. The vector diagram in Fig. 7 presents corresponding geometrical interpretation. Following to it the opposite trends in solvatochromic behavior may be explained by a specific orientation of the dipole moments $\vec{\mu}_g$ and $\vec{\mu}_e$, in particular, in MDPIPQ



Fig. 7. The vector diagram of MCPDPPQ, MDPIPQ and MPTNA dyes. The ground state moment $\vec{\mu}_g$, excited state moment $\vec{\mu}_e$ and their vector difference $\vec{\mu}_e - \vec{\mu}_g$ as calculated within the semiempirical PM3 method.

and MPTNA dyes the vector difference $\vec{\mu}_e - \vec{\mu}_g$ is close to be parallel with $\vec{\mu}_e$ and nearly antiparallel with $\vec{\mu}_g$. Comparing the calculated and measured solvatochromic slopes for the first optical absorption band, being defined by $\vec{\mu}_g(\vec{\mu}_e - \vec{\mu}_g)/a_0^3$, one must mention rather good agreement for both dyes. However, in regards to other value $\vec{\mu}_e(\vec{\mu}_e - \vec{\mu}_g)/a_0^3$, which defines the solvatochromic shift of the fluorescence band, the quantitative discrepancy between the experiment and theory must be admitted. The experiment reveals much stronger solvatochromic red shift indicating thus on considerably larger dipole moment of the excited state $(|\vec{\mu}_e|)$ involved into a fluorescence emission, especially in MDPIPQ dye. One must be emphasized, that the dipole moments have been calculated in the GP, not for the solvated phase which are the conditions of the experiment. In addition, after the excitation the nature of the lowest excited state, and accordingly its dipole moment $\vec{\mu}_e$, may be subjected to significant modification if the solvent and/or molecular geometry relaxations lead to situations when: i) other strongly polar excited state of solute becomes in solvent the lowest excited singlet (fluorescent) state or ii) initially locally excited state appears to be strongly modified due to solvent-dependent CI between configurations of this and highly polar intramolecular charge transfer (ICT) states, see e.g. Ref. [31,32]. To treat the problem properly, a program which includes the solvation energy in the Hamiltonian should be used. On the other hand, the fluorescent moment M_{fl} exhibits rather weak F-dependence (see Table 1) for all dyes thus the electronic structure and molecular conformation of the fluorescent excited state should not change substantially if the solvent polarity changes from CHX to ACN. Considering these facts together one may conclude that significant modification of lowest excited fluorescent state should occurs already on a route from the GP to a weakly polar CHX.

5. Conclusion

In conclusion we have reported here the measured optical absorption and fluorescence spectra as well as the basic photophysical characteristics of newly synthesized five-membered MDPIPQ and seven-membered MPTNA dyes being obtained from the same starter compound MBPDPPQ (MCPDPPQ) via the cyclization reaction. The spectra have been recorded in the organic solvents of different polarity in order to analyze the change of the electronic structure caused by solvent-modified electron transfer interactions. The experimental results are compared with the quantum chemical calculations performed within the semiempirical method PM3. The geometry optimization of MCPDPPQ, MDPIPQ and MPTNA dyes, leads in each case to several equilibrium conformations in the ground state that differ each other mainly by angular orientations of their phenyl rings. Such states are characterized by the same or nearly the same total energies being separated by the energy barriers sizeable with the thermal energy $(k_B T)$ at T = 300 K. Accordingly, the rotational dynamics of the phenyl groups is characterized in each case by quite large angular amplitudes. For this reason the calculations of optical absorbtion spectra has been performed within the semiempirical calculations in combination with the MD simulations. Cyclization of MCPDPPQ into MDPIPQ or MPTNA is accompanied by a significant red shift of the first optical absorption and fluorescence bands. While the solvent polarity changes from CHX to ACN all the dyes exhibit the hypsochromic shift of the first absorption band and the bathochromic shift of the fluorescence band. These findings appears to be consistent with the Lippert-Mataga solvatochromic model. The semiempirical calculations in combination with the dielectric polarization model describe properly the hypsochromic trend in the solvatochromic behavior regarding the first optical absorbtion band and give a reasonable value as for the shift itself. Importantly, the solvatochromic

shift keeps the same trend and also exhibits similar magnitudes in the MD simulations at T = 300 K. This finding means that a rotational dynamics of phenyl rings indeed does not influence the hypsochromic trend of the solvatochromic shift of the first optical absorption band and only slightly modifies its magnitude. The different solvatochromic trends of the optical absorbtion and fluorescent bands are explained by specific orientations of the ground and excited state dipole moments. On the other hand, quantitative evaluations of the solvatochromic shifts give quite well agreement with the experimental data only in regards the optical absorption spectra of all the dyes. In the case of the fluorescence spectra the experiment suggests much larger state dipole moment of the excited fluorescent state comparing to the one which follows from the semiempirical calculations. Corresponding discrepancy is especially strong for MDPIPQ dye and is assumed to be related with a significant modification of the nature of the lowest excited singlet (fluorescent) state due to solvent and/or geometry relaxations in the excited state of molecules. All the dyes reveal substantial guantum yield in weakly polar solvents what may be of interest for the luminescent or electroluminescent applications. Depending on a solvent polarity they emit light in green-yellow range of the visible spectra.

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