Photoluminescence properties of new Zn(II) complexes with 8-hydroxyquinoline ligands: Dependence on volume and electronic effect of substituents

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\textbf{Highlights}

- Four novel 2-arylethenyl-8-hydroxyquinoline Zn(II) complexes have been synthesized.
- The aggregation behavior was investigated by \textsuperscript{1}H NMR, UV–vis and photoluminescence.
- The photophysical properties can be tuned by introducing different substituents.

\textbf{Abstract}

A series of 2-arylethenyl-8-hydroxyquinoline ligands (A\textsubscript{1}–A\textsubscript{4}) with a trimethoxyphenyl, naphthyl, 2-fluoro-4-bromophenyl and anthracenyl group and their corresponding Zn(II) complexes (B\textsubscript{1}–B\textsubscript{4}) were synthesized and characterized by means of \textsuperscript{1}H NMR, ESI-MS, FT-IR and elemental analysis. A\textsubscript{1} and A\textsubscript{4} were characterized by single-crystal X-ray crystallography. The aggregation behavior of zinc salt and ligands in solution was investigated by several techniques, containing \textsuperscript{1}H NMR, UV–vis and photoluminescence (PL). The electronic nature and volume of arylethenyl substituents affect the absorption wavelength, the emission color, fluorescence lifetime, fluorescence quantum yield and thermostability of Zn(II) complexes. The experiments corroborated that the properties of Zinc(II) complexes can be tuned by introducing different functional substituents.

Introduction

As it is well known, 8-hydroxyquinoline (HQ) is one of the excellent luminescent materials for organic light-emitting diodes (OLEDs) up to now, it can chelate many metal ions, and the corresponding complexes, namely metaloquinolates, possess high luminescent efficiency and quanta efficiency [1–3]. The photo-/electroluminescence and charge-transporting properties of these complexes can be changed by varying the central metal ion [4–6] and the ligand structure [7–9]. The above characters of metaloquinolates have effectively promoted the design and development of lots of HQ-based organic electroluminescence materials.
Recently, more and more research groups focus their attention on zinc bis(8-hydroxyquinoline) (ZnQ2) derivatives, because they can exhibit better injection efficiency, lower operating voltage, and higher quantum yields than the commonly used AlQ3 [12]. For example, Cui et al. [13] reported 2-substituted-8-hydroxyquinoline molecules with large conjugated groups and tuned their luminescence to yellow-light. In order to balance the transport rates and improve the device performance of OLEDs, Zeng et al. [14] succeeded in synthesizing two novel compounds bearing hole-facilitating carbazole units and electron-facilitating 8-hydroxyquinoline units and their respective zinc complexes. This suggests that substituents attached to the quinolinolate ligand may be used as a handle for tuning of the complex photophysical properties. The literature, however, provides spotty evidence supporting the correlation of the substituent properties with the photophysical properties of quinolinolate chromophores. In an effort to explore the magnitude of the substituent effect and its possible use in the emission color tuning in ZnQ2 complexes, four unique 2-arylethenyl-8-hydroxyquinoline ligands based on 8-hydroxyquinaldine were designed and several substituents with different electronic effects, such as trimethoxy group with an electron donating effect, naphthalene and anthracene groups with a large \(\pi\)-conjugation effect, and fluorine (F) and bromine groups (Br) with a strong electron withdrawing effect were introduced into 2-substituted moiety of the 8-hydroxyquinoline ligands via an ethenylene spacer. The inclusion of the ethenylene spacer was also motivated by a high degree of electronic communication between the ligand and the substituted aryl moiety (Ar) as well as avoiding a potential interaction of ortho-substituents on Ar with the Q-moiety in the case of directly attached aryl moieties (Q-Ar). ZnQ2 type complexes containing these 2-arylethenyl-8-hydroxyquinoline derivatives as ligands, were synthesized, and the photophysical properties of these complexes were studied. As outlined in Scheme 1, four unique ligands (A1–A4) and their corresponding Zn(II) complexes (B1–B4) were synthesized.

**Experimental section**

**Chemicals and instruments**

All of the chemicals were commercial available, and used without further purification. Elemental analyses were performed with an EA1110 CHNS-O CE elemental analyzer. All fluorescence measurements were carried out on an LS 50B Luminescence Spectrometer (Perkin Elmer, Inc. USA). All UV/vis absorption spectra were recorded on a Lambda 20 UV–vis Spectrometer (Perkin Elmer, Inc. USA). \(^1\)H and \(^{13}\)C NMR experiments were carried out on a MERCURY plus 400 spectrometer at resonance frequencies of 100.63 MHz. Thermogravimetry/Differential Scanning Calorimetry (TG/DSC) of the thermal analyses were conducted under nitrogen atmosphere at a heating rate 20 K min\(^{-1}\) with a Shimadzu TG/DSC 6300. Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane/methanol as mobile phase.

**Synthesis**

**General procedure for the synthesis of 2-arylethenyl-8-hydroxyquinoline (A1–A4)**

To a solution of 8-hydroxyquininaldine (10.0 mmol) in acetic anhydride (10 mL) was added the corresponding aldehyde (11.0 mmol). The mixture was heated under reflux for 20 h. After the mixture was cooled, it was subsequently poured into ice water (200 mL) and stirred overnight. The solid obtained was filtered and washed with water. The solid residue was recrystallized from CH2Cl2 to afford 2-arylethenyl-8-acetoxyquinolines. A solution of 2-arylethenyl-8-acetoxyquinolines (6.0 mmol) in pyridine (30 mL) was refluxed for 40 min, and then water (15 mL) was added. The reaction mixture was refluxed for 4 h. After the mixture was cooled, water (200 mL) was added to the mixture. The solid obtained was filtered and washed with water, and dried in vacuo to give compounds of A1–A4.

**Scheme 1.** Synthesis of ligands A1–A4 and Zn(II) complexes B1–B4.
Synthesis of (E)-2-[(3, 4-trimethoxy-phenyl)ethenyl]-8-hydroxyquinoline (A1). Yield: 82.3%, m.p. 119.7 °C; 1H NMR (DMSO-d6, 400 MHz) δ: 9.57 (s, 1H), 8.27 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 16.5 Hz, 1H), 7.81 (d, J = 8.6 Hz, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.42 (s, 1H), 7.39–7.35 (m, 2H), 7.08 (dd, J = 6.7, 2.2 Hz, 1H), 6.93 (d, J = 8.9 Hz, 1H), 3.91–3.72 (m, 8H); 13C NMR (DMSO-d6, 400 MHz) δ: 154.26 (d, J = 7.5 Hz), 152.38 (s), 151.97 (s), 142.37 (s), 137.96 (s), 136.21 (s), 128.79 (s), 127.30 (dd, J = 26.1, 16.2 Hz), 123.40 (s), 121.68 (d, J = 8.4 Hz), 120.08 (s), 117.64 (d, J = 4.5 Hz), 110.04 (d, J = 5.4 Hz), 107.77 (s), 61.51 (d, J = 11.6 Hz), 60.95 (d, J = 11.7 Hz), 56.05 (d, J = 11.8 Hz), ESI-MS m/z: 338.00 ([M+H]+); Elemental analysis: found (%) C: 71.41, H: 5.73, N: 4.09; calculated for (C20H20NO4): C: 71.20, H: 5.68, N: 4.15.

Synthesis of (E)-2-(2-naphthalen-2-yl-vinyl)ethyl]-8-hydroxyquinoline (A2). Yield: 85.6%, m.p. 163.9 °C; 1H NMR (DMSO-d6, 400 MHz) δ: 9.58 (s, 1H), 8.32–8.25 (m, 2H), 8.12 (s, 1H), 7.95–7.88 (m, 3H), 7.79 (d, J = 8.5 Hz, 1H), 7.59 (d, J = 16.2 Hz, 1H), 7.51 (s, 2H), 7.40–7.31 (m, 2H), 7.07 (d, J = 8.8 Hz, 1H), 13C NMR (DMSO-d6, 400 MHz) δ: 153.57 (s), 152.04 (s), 138.02 (s), 136.38 (s), 134.16 (s), 133.83 (s), 135.56 (d, J = 2.6 Hz), 128.52 (s), 128.24 (d, J = 7.5 Hz), 127.76 (s), 127.45 (s), 126.50 (s), 123.53 (s), 120.42 (s), 117.70 (s), 110.21 (s); ESI-MS m/z: 298.00 ([M+H]+); Elemental analysis: found (%) C: 84.91, H: 5.23, N: 4.79; calculated for (C19H17NO): C: 84.82, H: 5.08, N: 4.71.

Results and discussion

Structure description

Single-crystal X-ray diffraction study reveals that the neutral A1 molecule crystallized in P21/n space group and the asymmetric unit

<p>| Table 1 | Crystallographic data for A1 and A4. |</p>
<table>
<thead>
<tr>
<th>A1</th>
<th>A4</th>
</tr>
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<tbody>
<tr>
<td>Crystallographic formula</td>
<td>C20H19NO4</td>
</tr>
<tr>
<td>Mr (g mol⁻¹)</td>
<td>337.36</td>
</tr>
<tr>
<td>T (K)</td>
<td>123(2)</td>
</tr>
<tr>
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<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P21/n</td>
</tr>
<tr>
<td>a (Å)</td>
<td>7.9893(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>12.4352(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>16.9068(4)</td>
</tr>
<tr>
<td>β (°)</td>
<td>91.8911(2)</td>
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<tr>
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</tr>
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<tr>
<td>S</td>
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</tr>
<tr>
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</tr>
<tr>
<td>wR₂</td>
<td>0.0999</td>
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</table>

* R₁ = Σ||F̅|| - |F̅||/Σ||F̅||
* wR₂ = Σw(|F̅|^2 - |F̅|^2)^2/Σw(F̅)^2 |^1/2|
contains one of the formula units (Fig. 1). The dihedral angle (ca. 40.5°) between the quinolone and 2, 3, 4-trimethoxyphenethyl moiety indicates that the molecule is non-planar. The C–O bond length of 1.362(2)–1.437(2) Å is indicative of a single bond character. The C10–C11 bond distance is 1.331(2) Å characteristic of the double bonds of alkenyl groups. In the crystal structure of A1, there is an intramolecular hydrogen bond between the phenol –OH group and the pyridine N atom [O–N = 2.692(2) Å]. The intermolecular O···O hydrogen bonds [O···O = 2.994(2) Å] between the phenol –OH groups and the methoxy O atom interlink the adjacent A1 molecules to form a supramolecular chain. As shown in Fig. 2, the quinolone rings of adjacent chains stack with each other, and the centroid-centroid distances are about 3.62 Å, indicating face-to-face π–π attractive interaction. Additionally, the weak intermolecular nonclassical C–H···O hydrogen bond [C···O = 3.411–3.439 Å] between the quinolone rings and the methoxy O atoms also play a vital role in the consolidation of the overall crystal structure with herringbone-like molecular packing (Fig. 3).

Single-crystal X-ray diffraction study reveals that the neutral A4 molecule also crystallized in P21/n space group and the asymmetric unit contains one of the formula units (Fig. 4). The dihedral angle (ca. 55.6°) between the quinolone and anthracene moiety indicates that these two moieties are not coplanar. The C10–C11 bond distance is 1.332(2) Å, in agreement with that found in A1 and characteristic of the double bonds of alkenyl groups. In the crystal structure of A4, each two adjacent A4 molecules belong to one stacking pair which stacking to each other in an edge-to-face fashion. Three C–H···π interactions with the H···centroid distances ranging from 2.61 to 2.97 Å are found between the flanking anthracene moieties and the quinoline rings (Fig. 5). Additionally, the weak intermolecular nonclassical C–H···O hydrogen bond [C···O = 3.405 Å] between the anthracene moieties and phenol –OH groups also play a vital role in the consolidation of the overall crystal structure with offset molecular packing (Fig. 6).

Coordination studies in solution

The coordination behavior of Zn(OAc)2·2H2O and A1 in solution was first investigated by 1H NMR spectroscopy (Fig. 7). In the 1H NMR spectrum of A1, the proton signals at 9.57, 8.27, 8.00, 7.81, 7.50, 7.42, 7.39–7.35, 7.08, 6.93 ppm can be easily assigned to each the corresponding hydrogen, which indicates the presence of the hydroxyquinoline and vinylene. The proton signal at 9.57 ppm corresponds to H–O proton of the quinoline. One doublet at 8.00 ppm with a coupling constant of 16.5 Hz, indicates the presence of the trans configuration in the vinylene units. Upon mixing 2:1 molar ratio of A1 and zinc salt in DMSO-d6, the resonance at 9.57 ppm corresponding to H–O proton of the quinoline gradually disappeared after 45 min. With the passage of time, the resonances in the pyridyl ring of quinoline shifted downfield while the resonances in the phenoxy ring shifted upfield with respect to that of the free
ligand. These results indicate the occurrence of the coordination between the ligand \( A1 \) and Zn(OAc)\(_2\). However, the complexes \( B2, B3 \) and \( B4 \) exhibit poor solubility and thus it is impossible to obtain any information on the aggregation behavior of \( A2, A3 \) and \( A4 \) in solution.

In order to further investigate the interaction mode of ligands with Zn\(^{2+}\) ion, the coordination reaction of ligands with Zn\(^{2+}\) ion was monitored through a UV–vis spectroscopic titration (Fig. 8a). After the addition of Zn\(^{2+}\) ion, the peak of \( A1 \) at 219 nm exhibits hypochromism 16% for \( B1 \), while the peak of \( A1 \) at 311 nm showed significant bathochromism about 16 nm for the peak of \( B1 \) at 327 nm. The peak at 350 nm was found to become weak and disappear in the end in the presence of increasing amounts of Zn\(^{2+}\) ion; This phenomenon suggests an enhancement of the \( \pi \)-conjugation due to the bidentate complexation of the ligand \( A1 \) to the d\(^{10}\) spectroscopically inactive Zn\(^{2+}\) ion [16]; thus a new band at 410 nm can be observed in the absorption spectrum of complex \( B1 \). No differences were observed in the absorption spectrum after the 1/2 ratio of Zn\(^{2+}\)/\( A1 \), so this experiment clearly indicated the formation of \((\text{ZnL}_2)\) in.

As depicted in Fig. 8b, the peak shapes of \( A4 \) and its spectroscopic titration with Zn\(^{2+}\) ion are far more different from the \( A1 \) because of its anthracenyl group with a large \( \pi \)-conjugation effect. After the addition of Zn\(^{2+}\) ion, the peak of \( A4 \) at 252 nm showed hypochromism 17% for \( B4 \), while a smaller shoulder peak around 288 nm was formed in the presence of increasing amounts of Zn\(^{2+}\) ion; The special broad absorption peak around 396 nm of \( A4 \) was attributed to the intramolecular through-space interaction between the two large \( \pi \) systems (8-hydroxyquinoline and anthracene). [17] The characteristic broad peak at \( \sim \)330 nm of \( B4 \), similar to the peak at 410 nm of \( B1 \), is overlapped with the broad absorption peak at \( \sim \)396 nm.

The absorption wavelength of ligands (\( A1 \– A4 \)) and Zn(II) complexes (\( B1 \– B4 \)) were all listed in Table 2. As shown in Table 2, the absorption spectra of \( A1 \– A3 \) are characterized by a very intense \( \pi \– \pi^* \) absorption bands at around 300 nm accompanied by a less intense and broader band above 340 nm. The new bands of complexes (\( B1 \– B4 \)) are at 410, 417, 420 and 430 nm, respectively, which are attributed to the charge transfer from metal to ligand band (CTML). Introduction of an anthracenyl group with a large \( \pi \)-conjugation effect in the complex of \( B4 \), results in the lowest energy absorption (430 nm). While introduction of electron-donating group (trimethoxyl) in the complex of \( B1 \) leads to the highest energy absorption (410 nm). When the electron-with drawing
group (F and Br) was introduced into the complex of B3, the CTML band shifts to 420 nm. It is surprising that the CTML band of B2 is 417 nm, which is shorter than that of B3, though the conjugation of the main ligand is enlarged. These variations of CTML bands support the conclusion that substituents with different electronic effects and different conjugation extent can evidently affect the CTML state of the complexes.

**Photophysical properties**

Results from the UV–vis spectrophotometric titrations were corroborated by the fluorescence spectroscopic titration (Fig. 9). Fluorescence photographs (Figs. 9 and 10) were obtained under irradiation of UV light (320 nm). As for ligand A2, addition of Zn\(^{2+}\) ion produced a clear growing yellow band at 583 nm accompanied by a band at shorter wavelength (460 nm) with the presence of clear isoemissive points. The presence of an isoemissive point indicates that at least two excited species are involved in the emission spectra [18–19]. In fact, the observation of an isoemissive point is a clear indication that two emitting species are present in equilibrium in the reaction mixture, possibly the free ligand and its Zn complex. The stoichiometry of the metal: ligand ratio and the continuous variation methods was found to be 1:2 for B1–B4.

The photophysical properties of B1–B4 such as emission maximal wavelength (\(\lambda_{\text{em}}\)), fluorescence quantum yield (\(\phi_F\)) and average fluorescence lifetime (\(\tau\)) were all listed in Table 3. As shown in Table 3, all the four complexes emit yellow to reddish orange color in methanol solution with maximum emission peaks at 572 nm of B1, 583 nm of B2, 602 nm of B3, 606 nm of B4 respectively [20]. Due to the space effect and strong electron-donating effect of the methoxy group, Complex B1 gave the shortest emission wavelength (Fig. 10). A red shift of 34 nm was observed when the anthracene group instead of the trimethoxy–phenyl group was introduced into the complex B4. The emission energy of these complexes B1–B4 appears to follow the same trend as the absorption energy of the CTML band [21].

In order to further understand the fluorescent properties of Zn(II) complexes B1–B4, their lifetimes were investigated in the solid state (Fig. 11). The shortest fluorescence lifetime 27.6 ns of complex B3 can be mainly attributed to the heavy atom effect of Br atom. [22] The longest fluorescence lifetime 70.1 ns of complex B1 can be attributed to the special C–H \(\rightarrow\) O–C interactions in the solid state. The long lifetimes suggest that the emissions originate from intermolecular charge transfer state which is a stable and long-lived charge-separated state due to strong charge transfer interactions inhibiting efficiently the back electron transfer.

In addition, the fluorescence quantum yields (FPL) of Zn(II) complexes B1–B4 were calculated by comparing the integrated photoluminescence intensities and the absorbency values of Zn(II) complexes with the references quinine sulfate [24]. Quinine sulfate (literature \(\phi_{ST}=0.55\)) was dissolved in 0.5 M H\(_2\)SO\(_4\) (refractive index (\(\eta\)) of 1.33). The samples were dissolved in THF (\(\eta=1.43\)). The absorbency was controlled < 0.05 for the samples and quinine sulfate. The fluorescence quantum yield was calculated using the below equation: 

\[
\phi_F = \phi_{ST} \frac{A_{ST}}{A_S} \frac{F_S}{F_{ST}} \frac{\eta_{ST}}{\eta_S}
\]

Where is the fluorescence quantum yield, \(A\) is the absorbency, \(F\) is the integrated photoluminescence intensity, is the refractive index of the solvent, \(S\) is sample, \(ST\) is the standard of quinine sulfate (\(\phi_{ST}=0.55\)). Based on the equation, the fluorescence quantum yields are calculated as 9.78%, 14.16%, 4.55% and 20.25% for B1, B2, B3 and B4 in THF, respectively. The fluorescence quantum yield of B3 is the lowest. This is presumably due to the heavy atom effect of Br atom which enhances intermolecular crossings and increases the chances of crossing from the singlet to the triplet state, ultimately...
In comparison with the complexes B1 and B3, the complexes B4 and B2 showed more high fluorescence quantum yields of 20.25% and 14.16%. The reason is that the large planer conjugative structures of the naphthalene and anthracene units may prevent intramolecular fluorescence quenching or non-radiative decay. Therefore, there is always an increase in $\phi_s$ with the extension of the conjugation system [23].

**Thermostability analysis**

The thermal properties of Zn(II) complexes were investigated by thermogravimetric analysis [26,27]. For TG measurement (Fig. 12), the sample was heated in the range of 25–1000 °C at a heating rate of 10 °C min⁻¹ in nitrogen atmosphere. The TG curves of Zn(II) complexes showed that the complex B1 was thermal stable before 324 °C and the complexes B2 were thermal stable before 333 °C. The complex B3 underwent an accelerated weight loss, 13% weight loss of B3 from 361 to 410 °C. The weight loss was in agreement with the calculated amount of 5-Br-2-F group. The thermal analysis results indicated that the thermal stability of complexes B3 were better than that of complex B1, B2 and B4.

### Table 2

<table>
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<tr>
<th>Ligands</th>
<th>$\lambda_1$ (nm)</th>
<th>$\lambda_2$ (nm)</th>
<th>$\lambda_3$ (nm)</th>
<th>Complexes</th>
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<th>$\lambda_2$ (nm)</th>
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<td>396</td>
<td>B4</td>
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### Table 3
Photophysical data of complexes B1–B4.

<table>
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<tr>
<th>Complexes</th>
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<th>$\lambda_{em}$ (nm)</th>
<th>ns</th>
<th>$\phi_s$ (%)</th>
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<td>B2</td>
<td>310</td>
<td>583</td>
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<tr>
<td>B3</td>
<td>263</td>
<td>602</td>
<td>27.6</td>
<td>4.55</td>
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<td>B4</td>
<td>286</td>
<td>606</td>
<td>50.1</td>
<td>20.25</td>
</tr>
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</table>

**Fig. 9.** Fluorescence emission changes of A2 ($\lambda_{em}$ B3 = 310 nm) in methanol solution upon addition of Zn²⁺ ion (0–2 equiv).

**Fig. 10.** The normalized fluorescence spectra of Zn(II) complexes B1–B4.

**Fig. 11.** Fluorescence decay and fit curves of Zn(II) complexes B1–B4 in solid state.

**Fig. 12.** TG curves of Zn(II) complexes B1–B4 at a rate of 20 °C min⁻¹ under N₂.
Conclusion

In the present study the luminescence properties of four novel aryl substituted 8-hydroxy quinoline derivatives and their metal complex dyes with Zn(II) have been reported for the first time and a study of the variation of photophysical properties in the presence of substituents on the 8-hydroxyquinoline has been carried out. Most of the results obtained here for the substituents effect on luminescence are in close agreement with the earlier reports that an electron-donating substituent at position 2 of the 8-hydroxyquinoline ligand cause a blue shift in the complex emission and an electron-withdrawing group result in significantly red shift. However some interesting results are emerged from the present study. The large volume group of naphthalene and anthracene at position 2 seems to cause a red shift in the complex emission and enhance the fluorescence quantum yield to high extent. An extraordinary decline in the fluorescence lifetimes are observed when anthracene group is present at position 2, which can be attributed to the obvious intermolecular C–H⋯π interactions between the anthracene moieties in solid state.

Acknowledgements

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre. The CCDC number of A1 and A4 are 966500, 1012202, respectively. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Tel.: +44(0)1223 762911; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.11.029.

References

[15] (a) Bruker AXS, Madison, WI, 1999; (b) G.M. Sheldrick, SADABS 2.05, Empirical Absorption Correction Program, University of Göttingen, Germany, 1997; (c) SHELXTL 6.10, Bruker Analytical Instrumentation, Madison, Wisconsin, USA, 2000.