


Cite this: *RSC Adv.*, 2024, 14, 20278

# Photophysical properties of Pt(II) complexes based on the benzoquinoline (bzq) ligand with OLED implication: a theoretical study†

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In this study, we investigate photophysical properties of eight inorganic Pt(II) complexes containing the bzq (benzoquinoline) ligand for OLED applications using high-level density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. We explore the radiative and non-radiative relaxation constants ( $k_r$ ,  $k_{nr}$ ), spin-orbit coupling (SOC) matrix elements, and spectral properties. To ensure compatibility between the host and guest compounds, we determine the HOMO and LUMO energy levels, as well as the triplet excitation energies of the selected systems, and evaluate their efficiency for OLED devices. Our findings indicate that all systems, except for **2a** and **2b**, exhibit a small  $S_1$ – $T_1$  energetic gap ( $\Delta E \leq 0.60$  eV) and promising SOC matrix elements (25–93  $\text{cm}^{-1}$ ), leading to a significant intersystem crossing (ISC) process. These complexes also show promising radiative relaxation rates ( $k_r = \sim 10^{-4} \text{ s}^{-1}$ ) and high phosphorescent quantum yields ( $\Phi > 30\%$ ). Thus, our results confirm that six out of the eight selected Pt(II) complexes are promising candidates for use in the emitting layer (EML) of OLED devices as efficient green emitters.

Received 6th May 2024  
Accepted 12th June 2024

DOI: 10.1039/d4ra03334e

rsc.li/rsc-advances

## 1 Introduction

Organic light emitting diodes (OLEDs) have high ability to be used in flat-panel displays and solid-state lamps, and hence, the research for their development has increased during the last decades.<sup>1–5</sup> The performance of OLEDs is such that in these devices, singlet and triplet excitons are produced from the recombination of holes and electrons injected from adjacent layers, statistically in a ratio of 3 to 1.<sup>6,7</sup> Therefore, according to the spin-forbidden law of general fluorescent organic systems, the efficiency of these devices is limited to 25%. Of course, this situation changes in the presence of heavy metal complexes, and due to the spin-orbit coupling (SOC), the internal quantum efficiency can be increased to about 100%. Therefore, doped OLED devices (containing the phosphorescent host and guest compounds in the triplet emitting layer) play an important role in the research and application of efficient OLED devices.<sup>7</sup> In recent years, research on the development of OLED devices has focused on two aspects: color improvement, quantum efficiency through doping heavy metal complexes, and optimizing the structure of devices. In this regard, extensive efforts have been made to study heavy metal complexes, including platinum(II),<sup>8–11</sup> iridium(III),<sup>12–14</sup> and ruthenium(I),<sup>15,16</sup> with their impact on OLED systems. Also, choosing the appropriate host

and guest materials in the emissive layer is another important strategy to optimize the structure of these devices. The triplet emission from guest materials mainly originates from three excitation mechanisms: the direct electron-hole recombination on the guest layer, the transferring of singlet excitons from the host to the guest *via* Förster energy transfer, and the transferring of triplet excitons based upon the Dexter energy transfer from the host to the guest.<sup>17</sup> Recent studies have shown that more exciton generation would lead to a higher efficiency in the OLED devices.<sup>18,19</sup>

Platinum(II)<sup>9,10,20–22</sup> complexes are widely used as guest materials in the structure of OLEDs. These compounds, having the configuration of  $d^8$  electrons, exhibit a square-planar structure. Investigating the performance of platinum(II) complexes with different ligands for use in OLEDs has become an important topic for studying the effect of different polydentate ligands and other ligands on the efficiency of these guest compounds. These ligands are C<sup>N</sup> bidentate ligands including ppy and bzq. C<sup>N</sup> ligands, which could be connected to the metal center through the N atom of the pyridine ring (as the  $\pi$ -acceptor) and the carbon atom of the phenyl group (as the strong  $\sigma$ -donor). These cyclometalated platinum complexes have been previously reported to be quite promising for OLED devices.<sup>10,20,23</sup>

In this study, we have investigated the photophysics and optoelectronic properties of eight cycloplatinated complexes as candidates to be suggested for use in OLED devices (see Fig. 1). These complexes were previously synthesized and characterized by other groups, and their phosphorescence nature has been

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4ra03334e>



proved experimentally.<sup>24–28</sup> Nevertheless, the application of these systems to any optical device, such as an OLED or solar cell has not been addressed yet. To that end, we used a comprehensive quantum chemical calculation to determine whether or not they could be used as a dopant guest material in the emitting layer of an OLED device.

These complexes have a common bzq (7,8-benzo quinoliny) ligand, and two other ligands,  $R_1$  and  $R_2$ , differ according to Fig. 1. For clarity, we have divided these compounds into four families of **1–4** (a and b) based on the common  $R_1$  and  $R_2$  ligands, respectively.

## 2 Computational details

In this study, the density functional theory (DFT) and the time-dependent density functional theory (TD-DFT) based on the B3LYP functional<sup>29–31</sup> were employed to determine the ground and excited state properties, respectively. This methodology has been widely used<sup>10,11,32–35</sup> in studying the different aspects of organic and inorganic systems such as electronic structures,<sup>36–38</sup> excited-state properties,<sup>39–41</sup> and also OLED devices.<sup>42–46</sup> Thus, the ground and excited states of selected systems were optimized, and the required photophysical parameters were determined. The TZVP<sup>47</sup> basis set was employed for the platinum(II) and the cc-pVDZ<sup>48</sup> (or def2-SV(P)<sup>49</sup> basis set) was used for all other atoms. We used the def2-SV(P) basis set for geometry optimization, and to determine the electronic transition energies, oscillator strengths, *etc.*, the cc-pVDZ basis function was applied. The Turbomole (v. 6.3)<sup>50,51</sup> program was used to determine the optimized geometries of the ground and excited states, and also electronic transitions. We also used ORCA, (v. 5.0.4)<sup>52</sup> program to determine the spin-orbit coupling (SOC)<sup>53</sup> elements. Also, the Gaussian 16 (ref. 54) and Chemissian programs were employed for analyzing the electronic structures of our selected systems.

## 3 Results and discussion

### 3.1 Optimized geometries and electronic transition

The optimized geometries of the ground ( $S_0$ ) and the first triplet excited state ( $T_1$ ) for all were determined at the B3LYP level of theory. The optimized structures of all complexes at the  $S_0$

ground state are shown in Fig. 2. We also tabulated selected geometry parameters for **1a–2b** complexes, dealing with the central Pt atom in Table 1, and more information regarding other systems is presented in Table S1, ESI file.†

At the ground state ( $S_0$ ), the Nbzq-Pt bond length for all complexes lies in the range of 2.135–2.219 Å. Also, the  $C_1$ -Pt bond length is predicted to be in the range of 2.020–2.077 Å. From experimental results, the N-Pt and  $C_1$ -Pt bond lengths were reported to be in the ranges of 2.095–2.153 Å and 2.030–2.057 Å, respectively. These results confirm a good agreement between the geometry parameters of our theory and the reported experimental results.<sup>24–28</sup> Also, our theoretical ground state bond angles (such as  $C_1$ -Pt-N and  $C_1$ -Pt-S) in all complexes are comparable with corresponding experimental values, indicating that the selected theoretical model is sufficiently reliable for studying the selected systems.

According to Table 1, the dihedral angles of  $C_1$ -N-Pt/ $C_1$ -N-Pt-S and N- $C_1$ -Pt- $C_2$ /N- $C_1$ -Pt-P are predicted to be in the range of 170°–180°, indicating that all of the complexes preserve planarity around the central platinum atom, at the ground and  $T_1$  excited states.

In addition, a comparison between the  $S_0$  and  $T_1$  optimized geometries is presented in the ESI file (Fig. S1†). As shown, no alteration in the bzq region and Pt connections has been predicted in the  $T_1$  optimized geometry. In all of our systems, the  $T_1$  optimized structure is quite similar to that of the  $S_0$ , the only exceptions are **2a** and **2b** complexes, in which alterations in the orientation of  $R_2$  have been predicted upon  $T_1$  optimization. As no significant geometry alterations have been predicted following the  $T_1$  geometry optimization of other complexes, a low possibility for the crossing of the  $S_0$  and  $T_1$  potential energy surfaces could be expected and consequently, the radiative deactivation mechanism would be more pronounced than the non-radiative deactivations for these systems.<sup>55,56</sup>

To obtain further insights into the electronic structures and the electronic transition of our selected systems, the frontier molecular orbitals (FMOs) are analyzed. These results are also essential for studying the capability of our selected systems (as the guest materials) with a host compound in the construction of the emitting layer (EML) of an OLED device. The analysis of the corresponding orbitals along with the energy gap is shown in Fig. 3 (see also Table 2 and ESI† for more information).

Apart from **2a**, and **2b** complexes, the highest occupied molecular orbital (HOMO) of other complexes, is mainly located over the bzq ligand and has been assigned as a  $\pi$  orbital ( $\sim 75\%$ ) along with a significant contribution of 5d orbitals ( $\sim 25\%$ ) of platinum. It mainly possesses  $n_{(S)} + \pi_{(phenyl)}$  and  $n_{(S)} + \pi_{(pyridine)}$  in **2a** and **2b** systems, respectively. In addition, the LUMO electron density distribution in all systems was identified as the  $\pi^*$  orbitals of the bzq ligand. Moreover, HOMO–1 in two complexes of **1a** and **1b** was assigned as the Pt 5d<sub>z<sup>2</sup></sub> orbitals ( $\sim 85\%$ ), while in **2a–3c** systems, the HOMO–1 was assigned as the  $\pi$  orbital of the bzq and platinum 5d orbitals ( $\sim 70\%$ ). In the **4a** system, the HOMO–1 is mainly located over the phenyl ligand, contributing to the  $\pi$  orbitals of the ligand and 5d orbitals of Pt (see ESI† for more details).

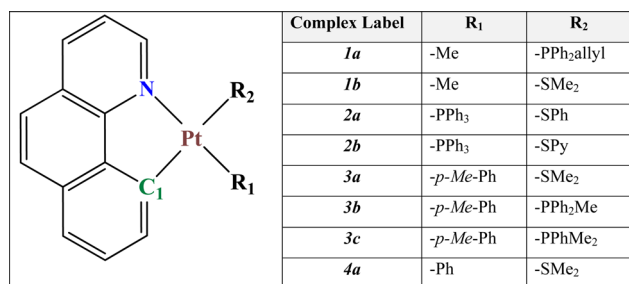


Fig. 1 Scheme of eight Pt(II) complexes based upon the bzq (on the left side) and different other ligands (right side,  $R_1$  and  $R_2$ ). Me, Ph, Py, and allyl, respectively stand for methyl ( $-\text{CH}_3$ ), -Phenyl ( $-\text{C}_6\text{H}_5$ ), Pyridyl ( $-\text{C}_5\text{H}_5\text{N}$ ), and  $-\text{CH}_2-\text{CH}=\text{CH}_2$  ligands.



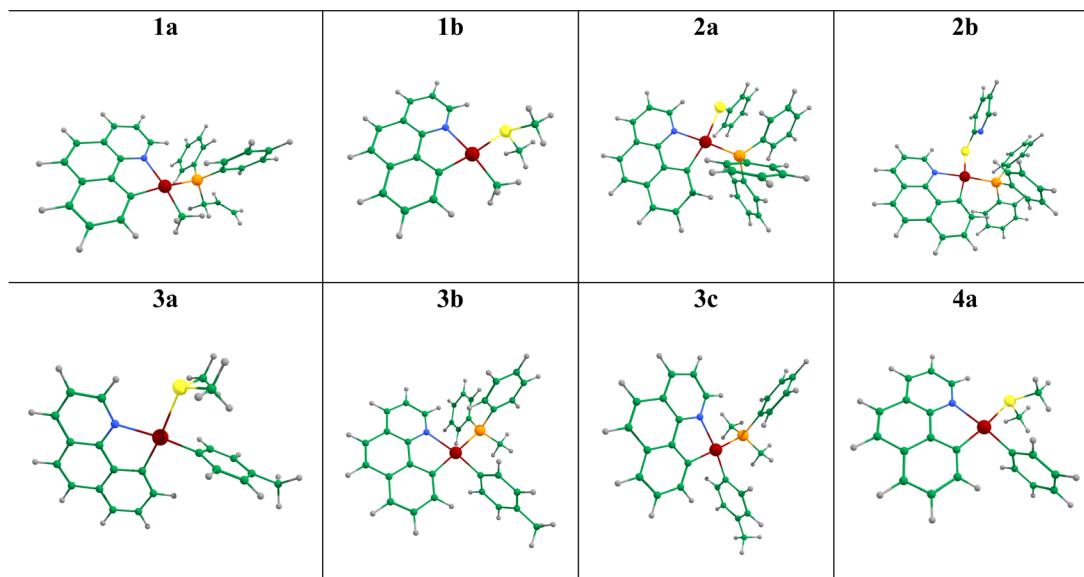


Fig. 2 The optimized structure of the  $S_0$  state of selected complexes, determined at the DFT/B3LYP/cc-pVDZ/def2-TZVP theoretical level.

According to our results, in complexes **1a**, **1b**, and **4a**, the transitions from HOMO to LUMO, being mainly related to the first singlet electron transition ( $S_1-S_0$ ), have the intra-ligand charge transfer (ILCT) mixed with metal-to-ligand charge transfer (MLCT) characters. For complexes **2a** and **2b**, according to the electron density distribution of HOMO and LUMO, the transition from HOMO to LUMO, corresponding to the  $S_1-S_0$  electronic transition, is assigned as a ligand-to-ligand charge transfer (LLCT) transition. In addition, in our selected systems, the HOMO–1 to LUMO single electronic transition could be assigned as the MLCT or ILCT transition.

As a result of changing the  $R_1$  ligand in **1b**, **3a**, and **4a** (containing the same  $R_2$  ligand), the electron density

distribution of HOMO exhibit decreasing trend over bzq and consequently slightly increase over central metal Pt(II). Nevertheless, the electron density distribution of the LUMO orbitals exhibits no significant change. Moreover, in **3a**, **3b**, and **3c** (having the same  $R_1$  ligand), because of the alterations in the  $R_2$ , the HOMO–LUMO energetic gap exhibits a slight increase. In both cases, we have also predicted an increase in the  $\Delta\text{add}^*$  indicating that the  $R_1$  ligands at **3b** and **3c** significantly lower the thermal relaxation rates.

The electronic transition energies and oscillator strengths of all selected Pt complexes were simulated based on the TD-DFT/B3LYP method. To compare with the experimental results of the literature, we have considered the implicit  $\text{CH}_2\text{Cl}_2$  solvent

**Table 1** Selected optimized geometry parameters of **1a–2b** complexes at the ground ( $S_0$ ), and the  $T_1$  electronic excited state, determined at the B3LYP level of theory. The experimental values obtained from the XRD method have been adopted from the literature.<sup>24–28</sup> The numbering of atoms is presented in Fig. 1. The  $C_2$ , P, S, and  $C_1$  indicate bzq carbon, phosphorus, sulfur, and  $-\text{CH}_3$  carbon atoms connecting  $R_1$  and  $R_2$  ligands to the central Pt

Complex	State	Bond length (Å)				Bond angle/degree			Dihedral angle/degree	
<b>1a</b>		<b>Pt–N</b>	<b>Pt–C<sub>1</sub></b>	<b>Pt–C<sub>2</sub></b>	<b>Pt–P</b>	<b>N–Pt–C<sub>1</sub></b>	<b>N–Pt–C<sub>2</sub></b>	<b>C<sub>1</sub>–Pt–P</b>	<b>C<sub>1</sub>–N–Pt–P</b>	<b>N–C<sub>1</sub>–Pt–C<sub>2</sub></b>
	$S_0$	2.198	2.055	2.073	2.385	79.5	169.0	174.0	174.3	169.6
	$T_1$	2.190	2.027	2.084	2.418	80.6	164.2	170.7	175.4	174.4
	Exp. <sup>24</sup>	2.153	2.057	2.039	2.302	81.3	170.3	174.1	—	—
<b>1b</b>		<b>Pt–N</b>	<b>Pt–C<sub>1</sub></b>	<b>Pt–C<sub>2</sub></b>	<b>Pt–S</b>	<b>N–Pt–C<sub>1</sub></b>	<b>N–Pt–C<sub>2</sub></b>	<b>C<sub>1</sub>–Pt–S</b>	<b>C<sub>1</sub>–N–Pt–S</b>	<b>N–C<sub>1</sub>–Pt–C<sub>2</sub></b>
	$S_0$	2.186	2.020	2.057	2.440	80.5	173.1	174.2	180.0	180.0
	$T_1$	2.163	1.964	2.074	2.490	81.7	174.8	174.3	179.9	179.9
<b>2a</b>		<b>Pt–N</b>	<b>Pt–C<sub>1</sub></b>	<b>Pt–P</b>	<b>Pt–S</b>	<b>N–Pt–C<sub>1</sub></b>	<b>N–Pt–P</b>	<b>C<sub>1</sub>–Pt–S</b>	<b>C<sub>1</sub>–N–Pt–S</b>	<b>N–C<sub>1</sub>–Pt–P</b>
	$S_0$	2.135	2.075	2.299	2.441	80.0	176.6	170.2	176.7	174.1
	$T_1$	2.128	2.069	2.306	2.438	79.6	176.9	170.5	179.6	174.2
	Exp. <sup>25</sup>	2.095	2.043	2.228	2.369	80.8	175.1	170.7	—	—
<b>2b</b>		<b>Pt–N</b>	<b>Pt–C<sub>1</sub></b>	<b>Pt–P</b>	<b>Pt–S</b>	<b>N–Pt–C<sub>1</sub></b>	<b>N–Pt–P</b>	<b>C<sub>1</sub>–Pt–S</b>	<b>C<sub>1</sub>–N–Pt–S</b>	<b>N–C<sub>1</sub>–Pt–P</b>
	$S_0$	2.148	2.077	2.350	2.451	79.8	176.0	171.0	178.0	172.3
	$T_1$	2.093	2.050	2.319	2.421	80.9	174.4	169.8	179.2	174.1
	Exp. <sup>25</sup>	2.108	2.049	2.222	2.365	80.7	175.2	171.4	—	—



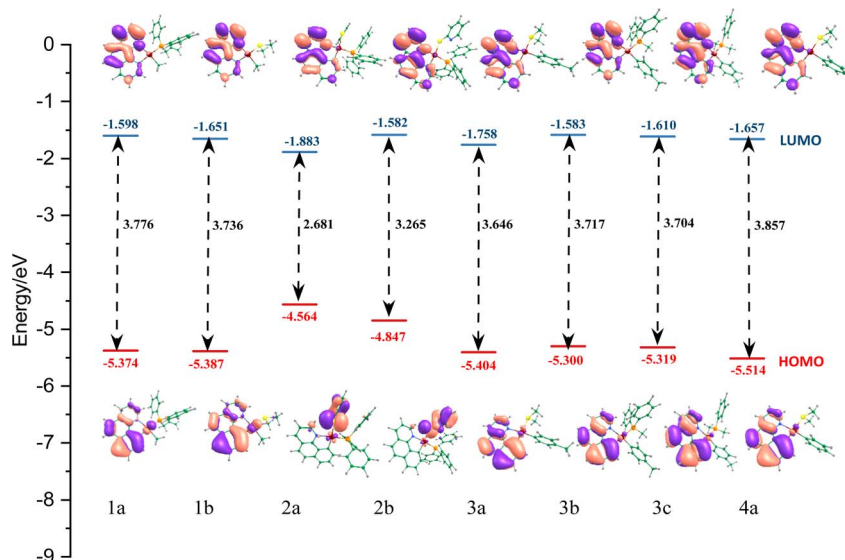


Fig. 3 Presentation of energy levels, energy gaps, and orbital composition distribution of HOMOs and LUMOs for our eight complexes. The energetic values are represented in eV.

model based on the COSMO algorithm implemented in the Turbomole program.<sup>57</sup> We considered more than 40 electronic transitions to cover the UV absorption of the selected systems within the range of 200–450 nm (corresponding to their experiments<sup>24–28</sup>).

In Fig. 4, we have presented the electronic transition energies of **1a** and **3a** systems with the experimental results from the literature.<sup>58,59</sup> In addition, we have presented several of the selected electronic transitions of **1a** in Table 2. As shown in Fig. 4, Table 2, and also in the ESI file,<sup>†</sup> in all selected systems there are two strong bands in the UV absorption, the first in the high-energy region of the spectrum roughly around 240 nm and the second around 320 nm. In both cases, two strong electronic bands were well matched by their experimental results.

In complex **1a**, the first transition band (~240 nm) corresponds to the  $S_{39}-S_0$  single electronic transition, having the largest magnitude of oscillator strengths (0.3475). It could be assigned as the  $^1\pi\pi^*$  transition with the contribution of bzq ( $\pi$ ) and  $-PPh_2C_3H_5$  ( $\pi^*$ ) ligands. The second strong transition band (~320 nm) corresponds to another  $^1\pi\pi^*$  transition, which is mainly a local bzq transition with a slight contribution of  $-PPh_2C_3H_5$  ligands in the  $\pi^*$  orbital (corresponding to  $S_5-S_0$  in **1a**). Thus, both of these two strong electronic bands could be assigned as the  $^1LLCT$  (ligand-to-ligand charge transfer) and the  $^1ILCT$  (inter-ligand charge transfer) transitions. Also, in **2a**, the  $\pi$  orbitals of the  $-SPh$ , and bzq ligands and the  $\pi^*$  orbitals of the  $-PPh_3$  ligand have the most important contributions in the first strong band (240 nm) which could be assigned as a  $^1LLCT$

Table 2 Selected electronic transitions and transition assignments for complex **1a** determined based on the TD-DFT/B3LYP theoretical model in the  $CH_2Cl_2$  implicit solvent model. For clarity, only transitions having oscillator strengths ( $f$ ) larger than 0.05 have been presented

State	Major contribution (%)	$\Delta E/eV$	$f$	$\lambda/nm$	Assignment
$S_3$	H-2 $\rightarrow$ L (66.8%)	3.615	0.0790	342.9	$^1MLCT/^1ILCT/^1LLCT$
$S_5$	H $\rightarrow$ L+1 (63%)	3.867	0.1804	320.6	$^1ILCT/^1LLCT/^1MLCT$
	H-1 $\rightarrow$ L+1 (14%)				
$S_{12}$	H-4 $\rightarrow$ L+1 (25.9%)	4.337	0.1005	285.9	$^1LLCT/^1ILCT/^1MLCT$
	H-3 $\rightarrow$ L+1 (14.1%)				
$S_{16}$	H-3 $\rightarrow$ L+1 (62.9%)	4.515	0.0529	274.6	$^1ILCT/^1LLCT/^1MLCT$
$S_{31}$	H-2 $\rightarrow$ L+5 (22.4%)	4.971	0.0963	249.4	$^1MLCT/^1LLCT$
	H-6 $\rightarrow$ L+1 (10.5%)				
$S_{32}$	H-1 $\rightarrow$ L+6 (56.8%)	4.984	0.0608	248.8	$^1MLCT$
	H-2 $\rightarrow$ L+5 (12.2%)				
$S_{34}$	H-3 $\rightarrow$ L+3 (34.2%)	5.050	0.0538	245.5	$^1LLCT/^1MLCT$
	H $\rightarrow$ L+5 (11.7%)				
$S_{35}$	H-4 $\rightarrow$ L+2 (34.1%)	5.103	0.0625	242.9	$^1LLCT/^1ILCT/^1MLCT$
	H-3 $\rightarrow$ L+4 (12.7%)				
$S_{39}$	H-12 $\rightarrow$ L (21.3%)	5.164	0.3475	240.1	$^1ILCT/^1LLCT/^1MLCT$
	H-3 $\rightarrow$ L+3 (20.9%)				
$S_{41}$	H-12 $\rightarrow$ L (44.7%)	5.184	0.2563	239.2	$^1ILCT/^1LLCT/^1MLCT$



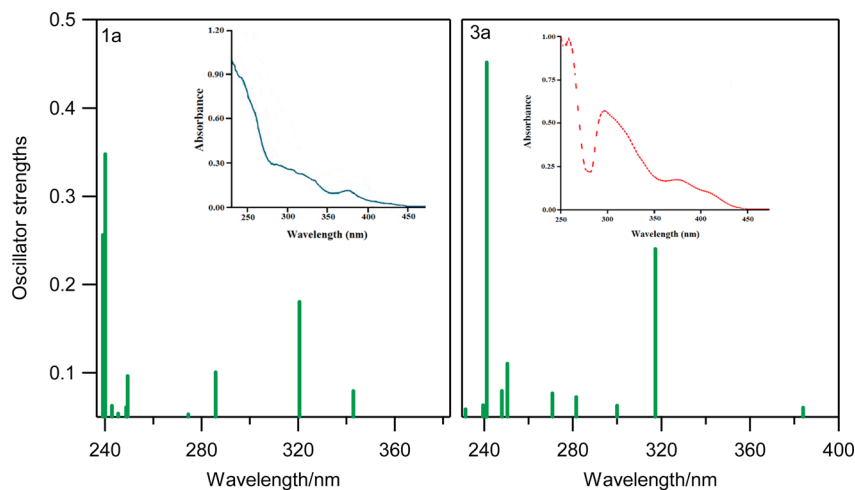


Fig. 4 The calculated UV absorption of **1a** and **3a** systems determined by the TD-DFT method (in the  $\text{CH}_2\text{Cl}_2$  implicit solvent model). The insets represent the corresponding UV absorption spectra adopted from the literature.<sup>24,25</sup>

electronic transition. The second band (320 nm) resulted from the single electron transition of the  $\pi$  orbitals (located over  $-\text{SPh}$ ) and bzq ligands to the  $\pi^*$  orbitals of the bzq ligand, owing to the  $^1\text{ILCT}$  and  $^1\text{LLCT}$  characters. We have discarded presenting further details regarding the assignments of electronic transitions in other complexes, as they are quite similar to **1a** (see ESI file†).

### 3.2 Phosphorescence efficiency and charge transport properties

To investigate the phosphorescence efficiency and analyze the thermal relaxation rate, the energy level of d-d\* transitions and the gap of d orbitals in our selected systems were investigated. The calculated values of  $\Delta\text{dd}^*$  (the energy difference between the highest occupied d orbital and the lowest unoccupied d orbital) and  $\Delta\text{dd}_{\text{occ}}$  (the energy difference between the two occupied d orbitals) in both the  $S_0$  and  $T_1$  levels are presented in Table 3. A larger  $\Delta\text{dd}^*$  has been established as more effective in rendering the d-d excited states thermally inaccessible. According to our results at both  $S_0$  and  $T_1$  levels, all complexes except **2a** and **2b** have a relatively low  $\Delta\text{dd}_{\text{occ}}$  value at the ground state ( $<0.20$  eV), which indicates a larger radiative relaxation

rate in these structures than in **2a** and **2b**. Also, the  $\Delta\text{dd}^*$  values for other complexes in both  $S_0$  and  $T_1$  levels indicate a high gap between occupied and unoccupied d orbitals. Therefore, thermal quenching is unlikely to occur due to this high energy gap.

Proper charge injection, charge transfer ability, and the balance between hole and electron transfer are crucial to the performance of OLED devices. To quantitatively evaluate charge injection for the studied complexes, the ionization potential (IP) and electron affinity (EA) in both the vertical and adiabatic forms were determined. The vertical IP is determined based on the ground-state optimized structures of neutral systems, while the adiabatic IP and EA are determined based on the optimized ionized structures. It is known that a lower IP facilitates hole injection, while a higher EA facilitates electron injection.<sup>10,20,60</sup> Also, the charge transfer character can be related to the spatial distribution of HOMO and LUMO orbitals. The IP and EA values are closely related to the energies of HOMO and LUMO, respectively. Additionally, the reorganization energy ( $\lambda$ ) was calculated for all structures to evaluate the characteristic of charge balance.

According to the Marcus theory, the charge-transfer rate could be estimated from the following equation:<sup>61–63</sup>

Table 3 The energetic levels of molecular orbitals and the values of  $\Delta\text{dd}_{\text{occ}}$  and  $\Delta\text{dd}^*$  (eV), determined at the B3LYP/def2-TZVP/cc-pVDZ level of theory

Complex	$E_{\text{HOMO}-1}$ (eV)	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$\Delta E_{\text{gap}}$ (eV)	$S_0$		$T_1$	
					$\Delta\text{dd}_{\text{occ}}$	$\Delta\text{dd}^*$	$\Delta\text{dd}_{\text{occ}}$	$\Delta\text{dd}^*$
<b>1a</b>	−6.533	−5.374	−1.598	3.776	0.159	6.313	0.088	6.651
<b>1b</b>	−5.527	−5.387	−1.651	3.736	0.140	6.213	0.256	5.923
<b>2a</b>	−5.662	−4.564	−1.883	2.681	1.098	3.645	0.647	4.111
<b>2b</b>	−5.584	−4.847	−1.582	3.265	0.832	3.947	0.252	4.502
<b>3a</b>	−5.480	−5.404	−1.758	3.646	0.076	3.646	0.337	4.104
<b>3b</b>	−5.439	−5.300	−1.583	3.717	0.139	6.045	0.003	6.025
<b>3c</b>	−5.449	−5.319	−1.610	3.704	0.130	5.906	0.392	6.075
<b>4a</b>	−5.576	−5.514	−1.657	3.857	0.062	5.944	0.219	5.967





**Table 4** Ionization potential (IP), electron affinities (EA), and reorganization energies ( $\lambda$ ) (eV) for selected complexes determined at the B3LYP/def2-TZVP/def2-SVP level of theory

Complex	IP <sub>v</sub> (eV)	IP <sub>a</sub> (eV)	HEP	$\lambda_h$	EA <sub>v</sub> (eV)	EA <sub>a</sub> (eV)	EEP	$\lambda_e$	$\Delta\lambda$	$k_{\text{HT}} \times 10^{14} \text{ (s}^{-1}\text{)}$	$k_{\text{ET}} \times 10^{13} \text{ (s}^{-1}\text{)}$
<b>1a</b>	6.67	6.30	5.48	1.19	0.19	0.34	0.51	0.31	0.88	1.89	2.63
<b>1b</b>	6.79	6.70	6.61	0.19	0.12	0.25	0.38	0.26	−0.07	1.76	15.74
<b>2a</b>	5.89	5.74	5.60	0.29	0.54	0.69	0.85	0.30	−0.01	1.54	3.27
<b>2b</b>	6.09	5.99	5.87	0.23	0.46	0.61	0.77	0.31	−0.08	1.51	8.69
<b>3a</b>	6.70	6.60	6.47	0.24	0.28	0.41	0.54	0.26	−0.03	1.65	8.59
<b>3b</b>	6.56	6.33	5.69	0.88	0.35	0.49	0.66	0.31	0.56	1.64	15.64
<b>3c</b>	6.60	6.39	5.80	0.81	0.31	0.49	0.65	0.33	0.47	1.60	14.78
<b>4a</b>	6.80	6.71	6.59	0.22	0.293	0.42	0.13	0.15	0.38	1.73	6.78

$$k_{\text{et}} = \frac{4\pi}{h} \frac{1}{\sqrt{4\pi\lambda k_{\text{B}} T}} \beta \exp \frac{-\lambda}{4k_{\text{B}}} \quad (1)$$

where  $\beta$  is the transfer integral or coupling matrix element between neighboring molecules. In addition,  $\lambda$  is the reorganization energy,  $k_{\text{B}}$  is the Boltzmann constant, and  $T$  is the temperature. Accordingly, a lower value of  $\lambda$  suggests a faster charge transfer process. The hole and electron rearrangement energies are determined from the following equation:<sup>64</sup>

$$\lambda_{\text{hole}} = \text{IP}_{\text{v}} - \text{HEP} \quad (2)$$

$$\lambda_{\text{electron}} = \text{EEP} - \text{EA}_{\text{v}} \quad (3)$$

All calculated values of IP<sub>v</sub> and EA<sub>v</sub> (v, stands to vertical), IP<sub>a</sub> and EA<sub>a</sub> (a, stands to adiabatic), hole extraction potential (HEP), electron extraction potential (EEP), and rearrangement energy for hole and electron ( $\lambda_{\text{e/h}}$ ) are listed in Table 4.

The results confirm that the IP values follow the trend of **2a** < **2b** < **3b** < **3c** < **1a** < **3a** < **1b** < **4a**, which corresponds to an increasing trend in HOMO energy. Also, considering EA, our selected systems exhibit the trend of **2a** > **2b** > **3b** > **3c** > **4a** > **3a** > **1a** > **1b**, which is in agreement with the decreasing trend of LUMO energy (see Fig. 2). Moreover, **2a** and **2b** with the highest EA and the lowest energetic level of LUMO would have better electron injection ability than other compounds, thus the highest charge transfer ability could be related to these two systems. In addition, in the **1a–4a** complexes, the rearrangement energy of electron transfer ( $\lambda_{\text{e}}$ ) and hole transfer reorganization energy ( $\lambda_{\text{h}}$ ) have almost the same values, indicating that selected systems are suitable for electron and hole transfer ideas.

Moreover, the fraction of triplet excitons ( $\chi_{\text{T}}$ ), is known as an important parameter against the non-radiative relaxation process *via* the Intersystem Crossing (ISC). The closer  $\chi_{\text{T}}$  to unity indicates the maximum rate of ISC and, consequently the higher possibility of radiative relaxation. The calculated values of  $\chi_{\text{T}}$  with details for selected systems are given in Table S5 (see ESI file†), all of which are in the range of 85–88%. These significant values of  $\chi_{\text{T}}$  indicate that the studied compounds have a high capacity for triplet-exciton production and thus a fast ISC process.

The effect of the R<sub>1</sub> ligand alteration in **1b**, **3a**, and **4a** has shown a decreasing trend in IP<sub>v</sub> and an increasing trend in  $\lambda_{\text{hole}}$  and EA<sub>v</sub>. Also, in **1b** and **4a**, an increase in IP<sub>v</sub>,  $\lambda_{\text{hole}}$ , and EA<sub>v</sub> is predicted, while  $\lambda_{\text{electron}}$  exhibits a decreasing trend. This indicates that the *p*-MeC<sub>6</sub>H<sub>4</sub> ligand (in **3a**) is accompanied by a better hole injection effect, and the *p*-Ph ligand (**4a**) improves the electron transfer rate. The injection of the electrons and the fraction of excitons are also improved in both cases. In addition, alterations in the R<sub>2</sub> ligand result in the lowering of the IP<sub>v</sub> and raising  $\lambda_{\text{hole}}$ , EA<sub>v</sub>, and  $\lambda_{\text{electron}}$  in **3a**, **3b**, and **3c**. Thus, it could be concluded that the *p*-P(Ph<sub>2</sub>) (Me) (**3b**) and *p*-P(Ph) (Me<sub>2</sub>) (**3c**) ligands significantly improve the electron and hole injection properties, and the *p*-P(Ph) (Me<sub>2</sub>) ligand (**3c**) increases the exciton generation fraction.

### 3.3 Emission properties, radiative decay rates, and OLED performance

In this section, the emission properties of the studied compounds are investigated based on the optimized geometry of the lowest triplet excited state (T<sub>1</sub>). The phosphorescent

**Table 5** Calculated triplet excited state transition energies along with the experimental phosphorescence results adopted from ref. 24–28

Complex	Major contribution (%)	$E$ (eV)	$\lambda$ (nm)	Assignment	$\lambda_{\text{exp}}$ (nm)
<b>1a</b>	L → H (77.9%)	2.28	543.8	<sup>3</sup> ILCT/ <sup>3</sup> MLCT	566
<b>1b</b>	L → H (79.8%)	2.35	527.6	<sup>3</sup> ILCT/ <sup>3</sup> MLCT	—
<b>2a</b>	L → H (99.0%)	1.83	677.5	<sup>3</sup> LLCT	572
<b>2b</b>	L → H (98.1%)	1.84	673.8	<sup>3</sup> LLCT	512
<b>3a</b>	L → H (81.7%)	2.23	556.0	<sup>3</sup> ILCT/ <sup>3</sup> MLCT	542
<b>3b</b>	L → H−1 (80.7%)	2.22	558.5	<sup>3</sup> ILCT/ <sup>3</sup> LLCT/ <sup>3</sup> MLCT	560
<b>3c</b>	L → H−1 (75.5%)	2.20	563.6	<sup>3</sup> ILCT/ <sup>3</sup> LLCT/ <sup>3</sup> MLCT	562
<b>4a</b>	L → H (81.7%)	2.23	556.0	<sup>3</sup> ILCT/ <sup>3</sup> MLCT	—



**Table 6** The phosphorescence quantum yield ( $\Phi_p$ ) of the considered eight complexes determined at the TD-DFT level of theory based upon the eqn (4)–(6) presented in the text

Complex	M%	SOC (cm <sup>-1</sup> )	<i>f</i>	$\Delta E_{S_1-T_1}$	$E_{T_1-P}$ (eV)	$k_r \times 10^{-3}$ (s <sup>-1</sup> )	$k_{nr} \times 10^3$ (s <sup>-1</sup> )	$\Phi_p$ (%)
<b>1a</b>	40.1	92.34	0.029	0.63	2.28	1.52	1.367	52.63 (0.17) <sup>a</sup>
<b>1b</b>	35.7	47.63	0.036	0.63	2.35	0.547	1.171	31.83
<b>2a</b>	11.8	25.52	0.075	0.40	1.83	0.517 (3.5 × 10 <sup>5</sup> ) <sup>a</sup>	3.470 (4.5 × 10 <sup>5</sup> ) <sup>a</sup>	12.96 (0.43) <sup>a</sup>
<b>2b</b>	17.3	35.72	0.022	0.38	1.84	0.270 (3.2 × 10 <sup>5</sup> ) <sup>a</sup>	3.427 (11.1 × 10 <sup>5</sup> ) <sup>a</sup>	7.30 (0.22) <sup>a</sup>
<b>3a</b>	29.4	46.66	0.060	0.53	2.23	1.09 (0.34 × 10 <sup>5</sup> ) <sup>a</sup>	1.526 (6.7 × 10 <sup>5</sup> ) <sup>a</sup>	41.64
<b>3b</b>	23.4	51.03	0.035	0.50	2.22	0.718	1.561	33.34
<b>3c</b>	21.7	43.74	0.047	0.51	2.20	0.742	1.600	31.67
<b>4a</b>	41.4	51.03	0.058	0.51	2.23	1.29	1.526	45.80

<sup>a</sup> The experimental data have been reported based on the solid-state phase.

properties of all the selected systems were computed, and the results including the lowest emission transition ( $T_1-S_0$ ), along with corresponding experimental results adopted from the literature, are presented in Table 5 (further information regarding molecular orbitals is presented in the ESI file†).

Concerning the  $T_1-S_0$  emission properties of our systems (Table 5), it is shown that phosphorescence emission from the lowest triplet excited state for all complexes is in the best agreement with the previously reported experimental results.<sup>24–28</sup> The results show that our selected complexes are phosphorescent systems emitting radiation within the range of 532–564 nm (in the green range of electromagnetic radiation). As stated before, the LUMOs in all complexes are localized on the bzq ligand, being assigned as the  $\pi^*$  orbital. Also, the HOMO is either a  $\pi$  orbital of bzq, with a significant contribution of the 5d orbital of Pt, or a  $\pi$  orbital located over the R<sub>2</sub> ligand (–Sph, –Spy). Thus, the phosphorescence emission from the  $T_1$  state to the ground (corresponding to the LUMO → HOMO transition), could be assigned in all of our complexes, apart from the **2a** and **2b**, as the <sup>3</sup>ILCT, <sup>3</sup>LLCT, and <sup>3</sup>MLCT transitions. In **2a** and **2b**, a quite low contribution of the central metal in the HOMO–LUMO was predicted.

The phosphorescence quantum yield ( $\Phi_p$ ) in OLEDs could be determined based on the radiative- and non-radiative relaxation rate constants ( $k_r$  and  $k_{nr}$ ):<sup>65</sup>

$$\Phi_p = \frac{k_r}{k_r + k_{nr}} \quad (4)$$

in this regard, the  $k_r$  and  $k_{nr}$  have been determined using the following equations:<sup>65,66</sup>

$$k_r(T_m \rightarrow S_0) = \frac{\eta^2}{1.5} E(T_m)^3 \left\{ \sum_n \frac{T_m |H_{SOC}| S_n}{E(S_n) - E(T_m)} \left( \frac{f_n}{E(S_n)} \right)^{\frac{1}{2}} \right\}^2 \quad (5)$$

$$k_{nr}(T_m \rightarrow S_0) \propto \exp\{-\beta[E(T_m) - E(S_0)]\} \quad (6)$$

where  $E(T_m)$  is the energy of the  $T_m$  to  $S_0$  transition,  $T_m |H_{SOC}| S_n$  is the spin-orbit coupling (SOC) matrix elements (here  $m$  and  $n$  are equal to 1), and  $\eta$  states the refractive index of the medium. In addition,  $f_n$  represents the oscillator strength and the  $E(S_n)$  is

the  $S_n$  to  $S_0$  transition energy. Given eqn (6), and according to the Kasha rule,<sup>67</sup>  $\beta$  is a parameter related to the structural distortion between  $T_1$  and  $S_0$  states, and  $[E(T_m) - E(S_0)]$  is the energy gap between the two corresponding states.<sup>22</sup>

The radiative rate constant ( $k_r$ ), could be essentially controlled by three factors, including the SOC, ( $T_1 |H_{SOC}| S_1$ ) matrix elements, the oscillator strength  $f_s$  in  $S_n$ , and the energy gap between the coupled states. Also, the matrix element,  $T_1 - |H_{SOC}| S_1$ , could be affected by various terms. The magnitude of the contribution of the metal ion ( $M\%$ ) in the relevant electronic transition could play an important role in the magnitude of the  $T_1 |H_{SOC}| S_1$  element. The larger  $M\%$  suggests a higher SOC and consequently a larger value of  $\Phi_p$ . Also, the smaller  $S_1-T_1$  energetic gap would suggest a larger radiative quantum yield. Another important parameter affecting the SOC element is the  $k_{nr}$  (non-radiative rate constant), which could be governed mainly by the magnitude of structural distortion following  $T_1$  optimization. It has been well established that the larger difference between the ground and excited state optimized geometry would suggest the larger possibility of non-radiative relaxation of the excited system and consequently a larger magnitude of the  $k_{nr}$ .<sup>68–70</sup> As stated supra, the optimized  $T_1$  structures of our selected systems are quite close to corresponding ground state geometries (see Fig. S1, ESI file†); thus, a low possibility for the non-radiative deactivation of these systems could be predicted.

The calculated values of SOC,  $M\%$ ,  $\Delta E_{S_1-T_1}$ ,  $E_{T_1-P}$ ,  $k_r$ ,  $k_{nr}$ , and  $\Phi_p\%$  determined from eqn (4)–(6), are listed in Table 6. The results show that the highest values of ( $M\%$ ) belong to the **1a**, **1b**, and **4a** systems, and the lowest values of ( $M\%$ ) relate the **2a** and **2b**. Moreover, the highest and the lowest magnitudes of the  $S_1-T_1$  energetic gap are related to **2b** (by 0.38 eV) and **2a** (by 0.40 eV), respectively. Hence, larger magnitudes of  $T_1 |H_{SOC}| S_0$  matrix elements were determined for the **1a**, **3a**, and **4a** complexes (92.34, 51.03 and 51.03 cm<sup>-1</sup>, respectively). Also, for the **2a** and **2b** cases, the corresponding values of  $T_1 |H_{SOC}| S_0$  matrix elements are determined to be quite low (25 and 35 cm<sup>-1</sup>, respectively). Additionally, large values for the  $k_r$  were found for **1b**, **3a**, and **4a** systems, while the lowest value is related to the **2b** complex ( $0.270 \times 10^3$  s<sup>-1</sup>).

Inspecting the effect of the R<sub>1</sub> ligand in **1b**, **3a**, and **4a** shows that  $M\%$  and SOC exhibit decreasing trends, but  $\Delta E_{S_1-T_1}$  shows



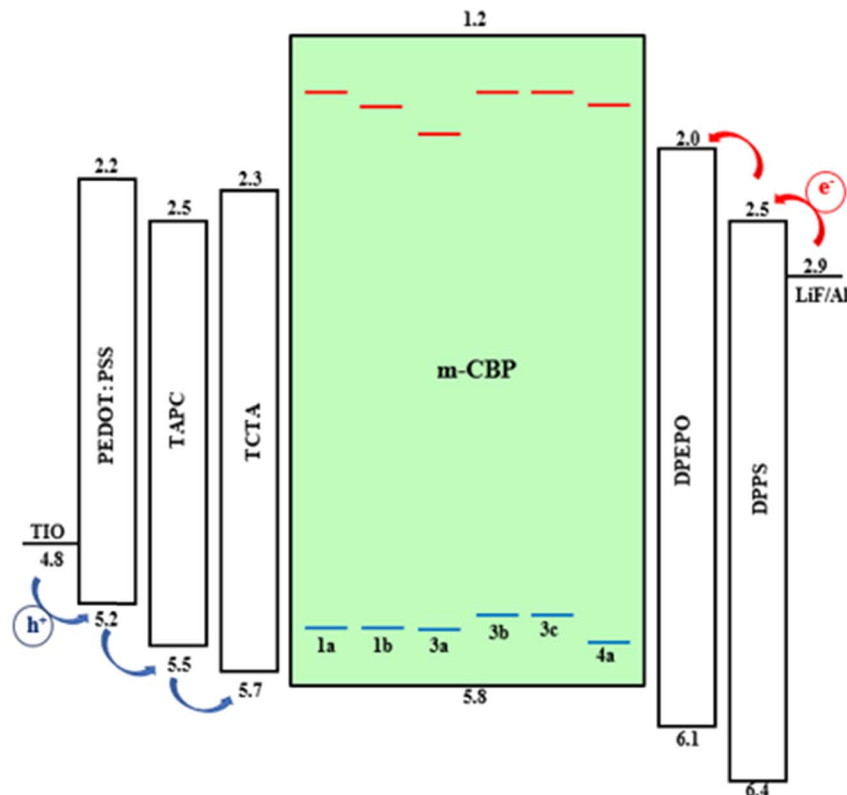


Fig. 5 Energy level diagram of materials proposed in this work in designing an OLED device.

an increasing trend. These alterations consequently increase the  $k_r$ . Also, in changing the ligand from  $-Me$  (in **1b**) to  $-Ph$  (in **4a**), an increasing trend in  $M\%$ , SOC and consequently in the  $k_r$  is predicted. This suggests that the two ligands of  $p-MeC_6H_4$  and  $-Ph$  have significantly improved effects on the optoelectronic properties of our studied complexes. In addition, in **3a**, **3b**, and **3c** (with the same  $R_1$  ligand), due to the change of the ligand in the **3a** structure to the **3b** and **3c**, there is a decreasing trend in the  $M\%$  and SOC and consequently  $k_r$ . Thus, it could be remarked that  $-P(Ph_2)$  ( $Me$ ) and  $-P(Ph)$  ( $Me_2$ ) ligands have a weakening effect on the emission performance of our complexes.

All the selected compounds (except for **2a** and **2b**), exhibit a good phosphorescent quantum yield of 32–52%. Thus, the results of this section and previous parts prove that almost all the studied structures are suitable candidates for use in OLED devices.

The compatibility between the guest and host materials is an important issue in studying the performance of OLED devices. After the charge generation and its flow, the charge balance and exciton confinement in the appropriate layer are very important in improving the efficiency of OLEDs. In general, a host material should have several fundamental properties. First, the triplet energy level ( $T_1$ ) of the host must be higher than that of the dopant to prevent the reverse energy transfer from the guest to the host. Secondly, for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the host is required to match the adjacent material layers so

that the hole and electron injections take place. To evaluate the suitability of the studied compounds in the structure of OLED, we propose a multi-layer OLED device, where the desired metal complexes are doped into the host material in the emission layer (EML). ITO and LiF/Al were used as the anode and cathode, respectively. Poly(3,4-ethylene dioxithiophene)/poly(styrene sulfonate) (PEDOT:PSS) has been proposed as the hole injection layer, and 4,40-(cyclohexane-1,1-dial) bis( $N,N$ -di- $p$ -tolylaniline) (TAPC) could be selected as a hole-transporting layer (HTL), tris(4-(9H-carbazol-9-yl)phenyl) amine (TCTA) could be used as an electron-blocking layer (EBL),<sup>71</sup> and 3,3'-di(9H-carbazol-9-yl)-1,1'-biphenyl (m-CBP) is suggested as a host in EML,<sup>72</sup> bis[2-(diphenylphosphine)phenyl]ether oxide (DPEPO)<sup>73</sup> as a hole-blocking layer (HBL) and diphenyl-bis(4-(pyridine-3-yl)phenyl)silane (DPPS) as an electron-transporting layer (ETL)<sup>74</sup> (see Fig. 5). The triplet energy of m-BCP as a host ( $T_1 = 3.18$  eV) is higher than that of our compounds as a dopant (according to Table 5). Also, from Fig. 5, it is seen that the HOMO levels of our complexes are higher than those of the host m-BCP, and their LUMO levels are lower than the corresponding LUMO level of the host; therefore, in all of our complexes, the doped compound will behave as hole and electron traps so that both electron and hole mobility in the EML will be retarded by the doping, and the device structure we used on six complexes is compatible. To conclude, we confirm that the Pt(II) complexes we analyzed in this study are promising candidates to be used in OLED devices, (except **2a** and **2b**).





## 4 Conclusion

The electronic structures, UV absorption spectra, phosphorescence properties, and other photophysical characteristics of eight cyclometalated Pt(II) complexes (**1a–4a**), each containing a bidentate bzq ligand and two additional ligands, were studied using DFT/TD-DFT methods. These compounds have been previously synthesized and characterized. Consequently, we investigated their photophysical properties for potential use in OLED devices. Our findings indicate that these systems exhibit good compatibility with other materials, such as m-BCP, TAPC, and DPPS. A small  $S_1-T_1$  energetic gap ( $\Delta E \leq 0.60$  eV) and promising SOC matrix elements ( $25\text{--}93\text{ cm}^{-1}$ ), leading to significant ISC processes, were predicted for all systems except **2a** and **2b**. These complexes also demonstrate large radiative relaxation rates ( $k_r \sim 10^{-3}\text{ s}^{-1}$ ) and high phosphorescent quantum yields ( $\Phi > 30\%$ ). Additionally, they show low electron and hole reorganization energies ( $\lambda_e < 0.30$  eV). Notably, except for **2a** and **2b**, all other systems predominantly emit in the green range of the electromagnetic spectrum (527–564 nm).

Based on these parameters, it can be concluded that all the selected systems, except for **2a** and **2b**, show considerable photophysical characteristics for utilization in optical devices such as OLEDs. For the **2a** and **2b** complexes, quite low values of SOC and phosphorescence quantum yield have been predicted; thus, we assume these two systems will be less favored for OLED applications. Furthermore, our study not only evaluates the potential of these new systems for OLED applications but also contributes to a deeper understanding of the photophysical characteristics of cyclometalated complexes based on the bzq bidentate ligand.

## Data availability

The data that support the findings of this study are available within the article and its ESI.†

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The support of the Research Council of the University of Isfahan is greatly appreciated. Also, the use of the computing facility cluster GMPCS of the LUMAT federation (FR LUMAT2764) is kindly appreciated.

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