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Organosulfur and Organoselenium Functionalized Benzimidazo[1,2-a] quinolines: From Experimental and Theoretical Photophysics to All-Solution-Processed OLEDs

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Abstract

In this study, we present the synthesis of benzimidazo[1,2-*a*] quinoline-based heterocycles bearing organosulfur and organoselenium moieties through transition-metal-free cascade reactions involving a sequential intermolecular aromatic nucleophilic substitution (SN_{Ar}). Both sulfur and selenium derivatives presented absorption maxima located around 355 nm related to spin and symmetry allowing electronic ${}^{1}\pi$ - π * transitions, and fluorescence emission at the violet-blue region (~440 nm) with relatively large Stokes shift. The fluorescence quantum yields were slightly influenced by the chalcogen, with the sulfur derivatives presenting higher values than the selenium analogs. In this sense, the quantum yields for selenium derivatives can probably be affected by the intersystem crossing or even the photoinduced electron transfer process (PET). The compounds were successfully applied in all-solution-processed organic light-emitting diodes (OLEDs), where poly(9-vinylcarbazole) was employed as a dispersive matrix generating single-layer device cells. The obtained electroluminescence spectra are a sum of benzimidazo[1,2-*a*]quinolines and PVK singlet and/or triplet emissive states, according to their respective energy band gaps. The best diode rendered a luminance of 25.4 cd·m⁻² with CIE (0.17, 0.14) and current efficiency of 20.2 mcd·A⁻¹, a fivefold improvement in comparison to the PVK device that was explained by a 50-fold increase of charge-carriers electrical mobility.

Keywords $OLEDs \cdot Organochalcogen \cdot Quinoline \cdot Fluorescence \cdot TDDFT \cdot Theoretical calculations$

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Introduction

Benzimidazo[1,2-a]quinoline compounds are a class of benzannulated benzimidazoles exhibiting a planar structure and a π -conjugated system that combined with proper functionalization possess biological and optical properties, such as antitumor [1, 2], anti-viral [3], antifungal [4], or antibacterial agents [5] and also as sensors for cations [6], and pH indicators [7]. Regarding their photophysics, these compounds present fluorescence emission tailored by the substituents, high quantum yields, and good thermal stability, becoming promising candidates for application in organic electronic devices [8], such as organic photovoltaics (OPV) [9, 10], organic field-effect transistors (OFET) [11], and thin-film transistors (TFTs) [12]. Moreover, seleniumcontaining compounds stand out in the building of organic light-emitting diodes (OLEDs), where several architectures are reported in the literature (Fig. 1) [13–18]. Among these compounds, highly efficient conventional and flexible



Fig. 1 Chemical structures of selected selenium-containing compounds for OLED applications: PSeZTRZ [13], (Se-PQ)₃-Ir [14], [(BSe)₂Ir(L)] [15], Ir-SeXF [16], P4 [17], and NSeD [18]

deep-red phosphorescent OLEDs were developed using the ambipolar selenophene-phenylquinoline-based Ir(III) complex [14]. Likewise, iridium(III) complexes containing a 2-(benzo[b]selenophen-2-yl)pyridine ligand were reported, showing deep red phosphorescence. In this study, these compounds were successfully used to fabricate white hybrid wet-processable light-emitting devices by mixing blue fluorescence, green thermally activated delayed fluorescence, and red phosphorescence [15]. For the same purpose, asymmetric heteroleptic Ir(III) phosphorescent complexes were reported and applied to develop electroluminescent (EL) materials, indicating the potential of selenium-containing groups in developing high-performance Ir(III) phosphorescent emitters [16].

Polymeric-based emitters are also reported for polymer light-emitting diode (PLEDs) applications in the NIR region, based on the copolymerization of a phthalimide-thiophene host polymer with a low-gap emitter containing the bis-thi enyl(benzotriazoloselenadiazole) unit [17]. In this context, Xue et al. described a NIR emitter based on the naphthoselenadiazole moiety (NSeD) for NIR-OLEDs, featuring a non-D-A structure with a very large HOMO/LUMO overlap [18]. This particular compound possesses a strong deep-red to NIR fluorescence and unique ambipolar character, thus contributing to a high external quantum efficiency.

The presence of heavier chalcogens in organic structures imparts different physicochemical/photophysical proprieties due to the element features (e.g. atom size, bond length, electronegativity, and polarizability) that might cause significant influence on their electronic structures by modulation of their nucleophilicity or electrophilicity, charge transport, intermolecular interactions, conformation, and crystallinity [19–22]. These different properties have been exploited from organic synthesis to medicinal and materials science [23, 24]. Taking these features into account, the present work proposes to characterize and explore the optical and electrooptical properties of some selenium-containing benzimidazo[1,2-a]quinolines as active layers of OLEDs. These promising features described above are combined with the easiness of manufacturing devices through solution deposition protocols. To do so, semiconductive polymers are attractive for the possibility of using them as hosts of small organic guest dyes [25, 26], combining the optoelectronic properties of both components, along with the production

of white organic light-emitting diodes (WOLEDs) [27–29]. Herein, we exploit the optoelectronic properties of singlelayer OLEDs using chalcogen benzimidazo[1,2-*a*]quinolines as guests of the polymeric host poly(9-vinylcarbazole) (PVK), implemented in very low quantities. These compounds were easily obtained showing great stability against air atmosphere, moisture, and temperature as well as fluorescence in the blue region with a large Stokes shift and a quantum yield dependent on the chalcogen. These characteristics led us to investigate their efficiency in OLEDs choosing sulfur- and selenium-containing derivatives to verify the influence of the chalcogen in such applications.

Experimental

Materials and Methods

Hydrogen Nuclear Magnetic Resonance (¹H NMR) and Carbon Nuclear Magnetic Resonance (¹³C NMR) spectra were recorded in CDCl₃ solutions on Varian 400 MHz or Bruker 400 MHz NMR spectrometers. Chemical shifts (δ) are given in part per million from the peak of tetramethylsilane ($\delta = 0.00$ ppm) as an internal standard in ¹H NMR or from the solvent peak of CDCl₃ ($\delta = 77.23$ ppm) in ¹³C NMR. Data are reported as follows: chemical shift (δ) , multiplicity, coupling constants (J) in Hertz, and integrated intensity. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), and m (multiplet). High-resolution mass spectra (HMRS) were recorded on a Micromass Q-Tof spectrometer, using electrospray ionization (ESI). Melting points were determined on a Büchi Melting Point M-545. Column chromatography was performed using silica gel (230-400 mesh). Thin-layer chromatography (TLC) was performed using silica gel GF254, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, stained with iodine vapor, or acidic vanillin. Air- and moisture-sensitive reactions were conducted in oven-dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry argon. Reagents and solvents were handled using standard syringe techniques. Dichloromethane of the spectroscopic grade was used in the photophysical characterization. UV-Vis absorption spectra were acquired on a Shimadzu UV-2450 spectrophotometer at a concentration of 10^{-5} M, and the steadystate fluorescence spectra were measured on an ISS single-photon counting spectrofluorometer model PC1. The maximum absorption wavelength (WL) was used as the excitation WL for fluorescence emission measurements. All measurements were performed at room temperature (25 °C). Fluorescence spectra in the solid state were measured with a Shimadzu spectrofluorometer RF5301 with a solid sample holder with an angle designed to limit the reflected excitation beam from the emission monochromator. For these experiments, the obtained materials were treated as powders.

Synthesis of 6-(phenylselenyl)benzo[4,5] imidazo[1,2-a]quinoline (3a-3c)

A mixture of 2-fluorobenzaldehyde **2** (1.2 mmol), 1*H*-benzo[*d*]imidazole **1a-1c** (1.0 mmol), and Cs_2CO_3 (3.0 mmol) in DMF (5.0 mL) was stirred at 80 °C for 8 h. After the end of the reaction, the mixture was cooled to room temperature and diluted with water. The resulting mixture was extracted with ethyl acetate. The combined organic layer was washed with water, dried over MgSO₄ and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography using hexane:ethyl acetate (9:1 v/v) as the eluent.

6-(Phenylselenyl)benzo[4,5]imidazo[1,2-a]quinoline (**3a)** Yield: 77%. Pale yellow solid. M.p.: 155–157 °C. ¹H NMR (400 MHz, CDCl₃) δ : 8.43 (d, *J*=8.5 Hz, 1H), 8.31 (d, *J*=8.2 Hz, 1H), 8.11–8.09 (m, 1H), 7.83–7.80 (m, 2H), 7.61–7.57 (m, 1H), 7.54–7.52 (m, 1H), 7.51–7.44 (m, 5H), 7.33–7.29 (m, 1H), 7.03 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ : 146.8, 144.5, 137.2, 134.1, 131.4, 130.1, 129.6, 128.7, 128.3, 127.9, 126.3, 125.3, 124.6, 124.2, 124.0, 123.1, 121.0, 115.1, 114.1. HRMS (ESI) calcd for C₂₁H₁₅N₂Se (M+H)⁺ requires 375.0395, found 375.0391.

6-(4-TolyIselenyI)benzo[4,5]imidazo[1,2-a]quinoline (**3b**) Yield: 78%. Yellow solid. M.p.: 151–153 °C. ¹H NMR (400 MHz, CDCl₃) δ : 8.41 (d, J=8.4 Hz, 1H), 8.29 (d, J=8.2 Hz, 1H), 8.08 (d, J=8.0 Hz, 1H), 7.67–7.69 (m, 2H), 7.59–7.55 (m, 1H), 7.51 (t, J=7.5 Hz, 1H), 7.46–7.43 (m, 2H), 7.31–7.25 (m, 3H), 7.00 (s, 1H), 2.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ : 146.8, 144.5, 139.8, 137.3, 134.1, 131.4, 130.9, 128.5, 128.3, 127.5, 125.7, 124.6, 124.2, 124.0, 123.0, 122.5, 121.0, 115.1, 114.1, 21.6. HRMS (ESI) calcd for C₂₂H₁₇N₂Se (M+H)⁺ requires 389.0551, found 389.0590.

6-(Phenylthio)benzo[4,5]imidazo[1,2-a]quinoline (3c) Yield: 65%. Yellow solid. M.p.: 145–148 °C. ¹H NMR (400 MHz, CDCl₃) δ : 8.48 (d, J= 8.5 Hz, 1H), 8.35 (d, J= 8.1 Hz, 1H), 8.11 (d, J= 8.0 Hz, 1H), 7.72–7.70 (m, 2H), 7.63–7.59 (m, 1H), 7.55–7.46 (m, 6H), 7.34 (t, J= 7.5 Hz, 1H), 6.94 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ : 146.2, 144.5, 135.6, 133.9, 131.4, 130.2, 130.0, 129.7, 129.5, 128.6, 128.5, 125.1, 124.7, 124.4, 123.7, 123.2, 121.2, 115.1, 114.1. HRMS (ESI) calcd for C₂₁H₁₅N₂S (M + H)⁺ requires 327.0950, found 327.0981.

Scheme 1 Synthesis of the chalcogen containing benzimidazo[1,2-*a*]quinolines 3a-3c



Theoretical Calculations

All calculations based on Density Functional Theory (DFT) and ab initio methods used in this work were performed with the quantum chemistry package ORCAv5.0.3 [30-32]. To confirm that the molecular models **3a-3c** represent global energy minima, initial geometries were obtained through conformational sampling via the semiempirical CREST software [33], with the ALPB implicit solvation module [34] simulating a dichloromethane environment. The most stable conformers were subsequently submitted to a relaxed scan and reoptimized using the ωB97X-D3 [35] /Def2-TZVP [36] level of theory with tight convergence criteria and the Conductor-like Polarizable Continuum Model (CPCM) [37] implicit solvation active. The resulting relaxed geometries have no imaginary vibrational modes and are considered to be true energy minima. Absorption spectra were obtained on the same ωB97X-D3/Def2-TZVP level of theory for the first 80 electronic transitions with Tamm-Dancoff approximation [38] active and the NBO 7 package [39] was used for canonical Kohn-Sham orbital analysis. Detailed analyses of transition densities and KS wavefunctions were performed using the MultiWFN [40] software and the inter-fragment charge transfer IFCT method. The vibrationally resolved electronic absorption spectra were studied using ORCA's S₀ and S₁ Hessians and the ezFCF software [41].

OLEDs Assembly

The OLEDs were fabricated in the configuration glassIITOIPEDOT:PSSIPVK:3a-3c (1.0% mol·mol⁻¹)|Ca|Al. ITO substrates (25 Ω ·cm⁻² from Delta Technologies) were cleaned using deionized water, 2-propanol, and acetone in an ultrasonic bath for 15 min for each solvent. Afterward, substrates were dried on a hot plate at 130 °C for 10 min and treated with UV ozone for 30 min. PEDOT:PSS was then deposited by spincoated (5000 rpm, 60 s) and annealed for 30 min at 110 °C. Next, a common solution of each benzimidazo[1,2-a]quinoline derivative and poly(9-vinylcarbazole) in THF was deposited $(2.6 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1})$ under controlled atmosphere environment $(N_{2(g)}, [H_2O] < 1 \text{ ppm}, [O_2] < 25 \text{ ppm})$ in a glove box system. Finally, calcium (30 nm) and aluminum (70 nm) were deposited by thermal evaporation at 5×10^{-6} mbar within a mBraun Evaporator. The relative concentration of the active layer was obtained by dissolving the derivatives in PVK, both from solutions with the same concentration $(2.6 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1})$ in a mixture ratio of 1.0 mol·mol⁻¹ in terms of solution volume. The optoelectronic properties of the OLEDs were evaluated using a 2400 Keithley SourceMeter, an OceanOptics USB2000+spectrometer, and a Konica Minolta CS-100A luminancimeter with a close-up lens No. 110, ϕ =40.5 mm, 10 to 20 cm. All data were collected simultaneously using a homemade LabView[®] interface.

Results and Discussion

Synthesis

In previous work, we described the synthesis and photophysical properties of chalcogen containing benzimidazo[1,2-*a*] quinolines [42]. The synthesis of the compounds is performed in a cascade process comprising an initial step of intermolecular aromatic nucleophilic substitution (S_NAr) of chalcogen benzimidazoles **1** with substituted 2-fluorobenzaldehyde (**2**) and the second step of intramolecular Knoevenagel condensation [43] (Scheme 1). The reaction is carried out in dimethylformamide with a slight excess of 2-fluorobenzaldehyde (1.2 eq.) and Cs_2CO_3 (3.0 eq.) as base affording the products **3a-3c** in 65–78% yield [42].

Optical Properties

The routine optical characterization of the benzimidazo[1,2a]quinolines **3a-3c** in solution was previously described in the literature [42]. We acquired their absorption and emission spectra once again for this particular work, using the absorption maxima as excitation wavelength. In Fig. 2 it can be observed that the chalcogen containing benzimidazo[1,2a]quinolines present an absorption maximum of around 350 nm, with electronic transitions related to ${}^{1}\pi$ - π *. It was also observed vibronic structures in the UV-Vis spectra, with wavenumber spacing for the observed vibronic progression of ~1,300 cm⁻¹. In addition, for all studied compounds, the most probable electronic transition is $0 \rightarrow 1$. These results agree with similar compounds reported in the literature [8]. The fluorescence spectra of **3a-3c** in solution present emission bands located in the violet-blue region (3a: 440 nm, 3b: 445 nm, and 3c: 440 nm), with relatively large Stokes shift and a structureless profile. Oppositely, in the solid state, the emission spectra of compounds 3a and 3c,



Fig. 2 UV–Vis absorption and steady-state fluorescence emission spectra (λ_{exc} =350 nm) of benzimidazo[1,2-*a*]quinolines **3a-3c** in dichloromethane (10⁻⁵ M)

used as models, depict structured vibronic progressions centered at ~475 nm (Figs. S11 and S12). As a general trend, the chalcogen does not affect the optical properties of the organic aromatic moieties. To understand the underlying reasons for this consistent behavior, theoretical calculations were performed to study the excited state dynamics of the systems.

The theoretical absorption and emission spectra that incorporate vibrational couplings were calculated for molecules **3a-3c** (Fig. S13). The resulting spectra are consistent with the experimental spectra depicted in Fig. 2 and capture the features that demonstrate that the first prominent transition band is not the most intense. Using the ezFCF software, an analysis of the three molecules indicated that the less intense and less energetic bands arise from a series of "hot bands" that are quite complex (Table S1). In these hot bands, the higher vibrational levels of the ground state become populated due to temperature effects before transitioning to the first electronically excited state. Additionally, we observed that the more intense bands originate from the $0 \rightarrow 1$ transition. Since compounds **3a-3c** have their characteristic molecular frames determined by two rotatable bonds X-(Se,S)-Y, where X and Y are the four condensed rings and the Ph/Ph-Me moieties, a conformational study was performed using a relaxed 360° dihedral scan (D) involving the two moieties. The DFT relative energy profile depicted

Fig. 3 360° relaxed dihedral scan rotating the (Se,S)-Y bond. Pink = Se or S, glassy light-blue = H or Me, gray = C, blue = N. Hydrogens omitted for clarity



in Fig. 3 suggests that all three molecules have two stable conformers appearing at $D = 0^{\circ}$ and $D \sim 120^{\circ}$ with energy differences of less than 1.6 kcal mol⁻¹. The semi-empirical conformational sampling using the CREST software confirms that the lowest conformer is the one appearing with $D=0^{\circ}$ with 77.6%, 63.4%, and 51.6% of the conformational distribution for **3a-3c** respectively. In essence, the conformational sampling confirms that the chemical environment is composed largely of the lowest, more stable, conformer (noted with a subscript "1" from now on) but, also, that the second lowest conformer (noted with subscript "2") may coexist with conformer 1 to some extent. The good agreement between experimental and theoretical vibronically resolved electronic spectra previously discussed supports the assumption that conformer 1 is the most relevant.

Upon ground state optimization, molecule $3a_1$ assumes a C_s symmetry, with its highest occupied molecular orbital (HOMO) distributed across the four condensed rings and the Se atom (Fig. 4), exhibiting an orbital delocalization index (ODI) of 10.02 [44]. Due to poor orbital superposition between moieties, there is no significant electronic probability density on the phenyl moiety (Table S2). Consequently, the calculated bond order for the Se-Ph bond (1.04) is smaller than that of the Se-(four condensed rings) group (1.16). The lowest unoccupied molecular orbital (LUMO) is primarily localized over the (four condensed rings)-Se moieties (ODI = 9.12), with only low electronic density observed on the phenyl group (Fig. 4). Compared to $3a_1$, the second lowest conformer, $3a_2$, displays greater asymmetry and belongs to the C1 point group. The HOMO predominantly spreads across the four condensed rings-Se moieties (ODI = 8.65); however, a more favorable atomic orbital superposition enables some probability density to extend to the phenyl moiety (Fig. 5). The LUMO of $3a_2$ (ODI = 10.04) visually resembles that of $3a_1$, with minor density present on the phenyl moiety.

Molecules $3b_1$ and $3b_2$ share considerable similarities with $3a_1$ and $3a_2$, respectively, with the only distinction being the addition of a methyl group in the *para* position to the phenyl moiety. This addition has a negligible impact on



Fig. 4 HOMO and LUMO orbitals for molecules $3a_{1,2}$, $3b_{1,2}$, and $3c_{1,2}$ with isosurface contour value = 0.05. Red and blue are used to depict negative and positive phases respectively. The NTO values (in blue) show the HOMO \rightarrow LUMO composition for the first electronic transition





the overall HOMO and LUMO distributions. The HOMO and LUMO ODI for $3b_1$ are 10.21 and 9.10, respectively, while for $3b_2$ they are 10.50 and 9.98. Remarkable resemblances are observed for molecules $3c_1$ and $3c_2$ and their selenium counterparts. In comparison to the selenium molecules, $3c_1$ and $3c_2$ exhibit analogous HOMO and LUMO distributions, with a marginally higher localization observed in $3c_1$ HOMO (ODI ~ 9.00) and a more delocalized LUMO in $3c_2$ (ODI = 10.20).

As already discussed, the compounds 3a, 3b, and 3c have two possible coexisting conformations with dihedral angles equal to 0° and ~120° in the electronic ground state (S_0) . When the geometry is optimized for the first excited singlet state (S_1) **3a**₁ experiences significant geometrical distortions (Fig. 5), especially relative to the Ph-Se- positions: dihedral angles change from 0° to 49.2°. This variation accounts for a low accuracy of the calculated S_0 - S_1 distance bond. For this calculated geometry, the S₁ energy is 84 kcal mol⁻¹ (3.65 eV) higher than the S₀ state. On the other hand, derivative $3a_2$ experiences a much less noticeable geometric change, going from an initial 120.7° dihedral to 131.8° with a total RMSD = 0.254 Å and 85 kcal mol⁻¹ (3.70 eV) increase in energy relative to the ground state. Molecule $\mathbf{3b}_1$ faced the largest geometric variations (Fig. 5) when optimized to S_1 , going from 0° to 49.4° in dihedral angle, and reaching RMSD = 0.868 Å compared to S₀. The electronic energy relative to the ground state is 84 kcal mol⁻¹ (3.64 eV), which is similar to what was observed for its $3a_1$ counterpart. The dihedral angle of $3b_2$ in the first excited singlet state changes from 121.3° in S₀

to 132.9° , the overall RMSD = 0.320 Å, and the energy increases by 88 kcal mol⁻¹ (3.81 eV) relative to S₀. Finally, molecule $3c_1$ changes its dihedral angle from ~0° to 48.4° and keeps the trend that the most stable (lowest) conformer undergoes large geometric changes under excitation to the S_1 electronic state with RMSD = 0.748 Å. Energetically the optimized $3c_1 S_1$ system is 86 kcal mol⁻¹ (3.72 eV) higher than the ground state. Finally, the $3c_2$ molecule changes its dihedral from 119.3° to 131.4° when optimized to the first excited state. The overall geometric change has RMSD = 0.240 Å and appears 88 kcal mol⁻¹ (3.84 eV) higher than the ground state. As previously noted, theoretical vibronically resolved absorption spectra predict the formation of hot bands at lower energies than the more prominent $0 \rightarrow 1$ band. However, the vibronic coupling methodology does not provide sufficient insight into the dynamics of the electronic densities and orbitals involved. To overcome this limitation, we conducted a traditional time-dependent density functional theory analysis using the ωB97X-D3 density functional in conjunction with Natural Transition Orbitals (NTO).

As expected, a pure TD-DFT approach does not identify the previously identified hot bands. However, the first TD electronic transition shows a good agreement with the vibronically resolved $0 \rightarrow 1$ absorption for each molecule (illustrated in Fig. S14). The full TD-DFT electronic properties for the studied molecules are summarized in Table 1, which includes the wavelength of the low-lying electronic transition, oscillator strength (f_{osc}), HOMO \rightarrow LUMO percentage contribution for the first excited state transition,

Table 1	TD-DFT	data	describing	low-lying	electronic	transition	fo
molecul	les 3a _{1,2} , 3	b _{1,2} , a	and $3c_{1,2}$				

Molecule	WL (nm)	f _{osc}	H–L transition (%)	$n \rightarrow \pi^*$ contribution (%)	CT (%)	
3a ₁	307.5	0.54	93	21	24	
3a ₂	299.6	0.46	92	20	32	
3b ₁	307.9	0.54	93	22	24	
3b ₂	300.3	0.46	92	27	41	
3c ₁	296.6	0.53	92	16	20	
3c ₂	298.4	0.51	92	11	22	

 $n \rightarrow \pi^*$ contributions, and charge transfer percentages (CT(%)). The electronic density difference based on the particle-hole formalism is used to visually analyze the transitions, illustrating behavior consistent with charge redistribution, and is related to the CT(%), which represents the percentage of electron transfer from one moiety to another during the transition. For a visual representation of the frontier orbitals, refer to Fig. 4, and for charge transfer, refer to Fig. 6. It is worth noting that the phenyl moiety has negligible participation in these processes.

OLED Assembly

The semiconductive polymer PVK has already been applied in the assembly of device cells because of its charge-carrier transport, mechanical, and processability characteristics. The high-energy bandgap of PVK affords the possibility of being used as an electron-blocking and hole transport layer at the same time, being an interesting host of small organic dyes [45]. The benzimidazo[1,2-*a*]quinolines **3a-c** were dispersed in PVK in the molar ratio of 1.0% mol·mol⁻¹ to the polymer solution. Figure 7 depicts the EL spectra of all composites as a function of bias. It is possible to assign the emission bands from the benzimidazo[1,2-*a*]quinoline derivatives around 430 nm by comparing these results with the experimental emission spectra in both solution (Fig. 2) and in the solid-state (Figs. S11 and S12). Diodes with **3a** and **3b** also showed a red band centered at $\lambda_{em} = 570$ nm which can be assigned to the PVK triplet state [46]. Besides, the contribution of PVK to the EL spectra of **3a** and **3b** makes the CIE coordinates shift towards the white region of the diagram (Fig. 7d).

Figures of merit of the OLEDs prepared using the PVK:**3ac** were obtained in terms of current density, brightness, and current efficiency versus voltage curves, and data is displayed in Fig. 8 and summarized in Table 2. As a general trend, these OLEDs exhibited very poor performances with better results obtained with the diode based on compound **3c**: $V_{on} = 7.5$ V, $L_{max} = 25.4$ cd·m⁻², and $\eta = 20.2$ mcd·A⁻¹. To understand the fundamental aspects involved in these low efficiencies, charge-carrier transport studies were performed in terms of electrical mobilities (μ), the total density of trap-states (N_T), and average trap energies (E_T), according to Mott-Gurney's space-charge limited-current (SCLC) model (fittings are in Fig. 8a), as described by Eq. (1) [47–49]:

$$J_{SCLC} = \frac{9}{8} \epsilon \epsilon_0 \mu \frac{V^2}{L^3} \tag{1}$$

where J_{SCLC} is the current density at the SCLC region, ϵ is the active layer dielectric constant (~3 for semiconducting polymers), ε_0 is the free-space electrical permittivity, μ is the electric mobility in the trap-filling SCLC region, V is the applied bias, and L is the active layer thickness (70 nm). All OLEDs based on compounds 3a-c present similar electrical mobilities values at the trap-filling processes $(5 \times 10^{-6} < \mu < 2 \times 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1})$, but a better performance in terms of charge carrier mobilities (10 to 1000 times higher), turn on (from 10 V to 7.5 V), and luminance (a four-fold improvement) in comparison with PVK-based active matrix [45]. In a global view, the OLED prepared with compound 3a exhibits better charge-carrier transport than the other ones (Table 2). Nevertheless, it is not possible to observe a clear correlation between the OLED figures of merit with the electrical mobility trends. Considering such trends, we investigate the total concentration of trap-states (N_T) and the average trap energy of these OLEDs, using the trap-filled-limit Voltage (V_{TFI}) relation [50, 51]:



Fig. 6 Electronic density difference (EDD) for the first electronic excitation. Pink represents electronic density lost (hole) and green represents electronic density gained. Isosurface value = 0.005



Fig. 7 Electroluminescence spectra of benzimidazo[1,2-*a*]quinolines **a** 3a, **b** 3b, and **c** 3c, and **d** their respective CIE chromaticity diagram as a function of applied bias

$$V_{TFL} = \frac{qN_T L^2}{2\epsilon\epsilon_0} \tag{2}$$

where q is the elemental charge. The obtained N_T values range in magnitude 10^{17} cm⁻³ (see Table 2), being large for the OLED based on the compounds **3a** and **3c**: 2.71×10^{17} and 3.38×10^{17} cm⁻³, respectively. However, a reasonable correlation of the OLED optoelectronic properties was generated when determining the average energy of those traps (E_T), using the Mark-Helfrich model [47, 50]. Poorer performances can be associated with the higher energy of the traps. E_T calculated for the poorer performance of OLED (**3a**) can be explained by the two times higher E_T values than for the other diodes (**3a**: 121 meV, **3b**: 59 meV, and **3c**: 67 meV). The OLEDs presented external quantum efficiencis (EQE) between 1.56×10^{-3} to 3.42×10^{-2} %.



Fig. 8 Optical-electronic properties of the devices are composed of compounds 3a-c. a Current density vs Voltage; b Luminance vs Voltage and c Current Efficiency vs Voltage

Table 2 Optical-electronic parameters obtained from the OLEDs

Compound	λ_{EL}	V _{on}	L	J ^a	η	CIE 1931 (x,y)	V _{TFL}	N _T	ET	μ	EQE (max)
3a	430, 570, 603	7.5	7.3	0.60	2.0	(0.29, 0.24)	4.0	2.71×10^{17}	121	1.58×10^{-5}	1.09×10^{-2}
3b	430, 570, 603	8.0	11.5	0.12	10.7	(0.31, 0.25)	3.5	2.37×10^{17}	59	5.74×10^{-6}	1.56×10^{-3}
3c	429, 603	7.5	25.4	0.17	20.2	(0.17, 0.14)	5.0	3.38×10^{17}	67	8.97×10^{-6}	3.42×10^{-2}

 λ_{EL} (nm) is the electroluminescence maxima, V_{on} is the turn-on voltage (V), L is the maximum luminance (cd·m⁻²), J is the current density (A·cm⁻²), η is the current efficiency (mcd·A⁻¹), V_{TFL} is the trap-filling Voltage (V), N_T is the total density of trap-states (cm⁻³), E_T is the average energy of the traps (meV), μ is the electrical mobility (cm²·V⁻¹·s⁻¹), and EQE (%) is the external quantum efficiency of OLEDs

^aCurrent density values at the maximum of luminance

Conclusions

The synthesis of benzimidazo[1,2-a]quinoline-based heterocycles bearing organosulfur and organoselenium was achieved in an efficient synthetic approach in good overall yields, in just two reaction steps, without using any transition metal catalysts, via a cascade reaction between the substituted chalcogen-1H-benzimidazoles and 2-fluoroarylaldehydes substrates. Theoretical calculations based on density functional theory confirmed the presence of two coexisting conformers for the studied compounds, with dihedral angles equal to 0 and ~120°. The first electronic transition described by TD-DFT appears as a mixture of charge transfer and local excitation involving only the four condensed ring-chalcogen moieties while the Ph/Ph-Me group remains mostly isolated in the process. Nevertheless, employing the benzimidazo[1,2-a]quinolines as guests of the PVK polymeric host matrix offered an improvement of the device only based on PVK, with higher charge carrier mobilities, and lower turn-on voltage. Hence, for their versatility and low-cost, the organochalcogen derivatives presented serve as promising alternatives for the construction of solutionprocessed devices.

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Authors' Contributions Rodrigo Borges da Silva: Formal analysis. Felipe Lange Coelho: Formal analysis, editing and review the manuscript. Henrique de Castro Silva Junior: Data Validation, formal analysis, editing and review the manuscript. José Carlos Germino: Formal analysis, editing and review the manuscript. Teresa Dib Zambon Atvars: Resources, editing and review the manuscript, funding acquisition. Fabiano Severo Rodembusch: Conceptualization, data validation, resources, editing and review the manuscript, funding acquisition. Luís Gustavo Teixeira Alves Duarte: Conceptualization, data validation, editing and review the manuscript. Paulo Henrique Schneider: Conceptualization, data validation, resources, editing and review the manuscript, project administration, funding acquisition.

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Declarations

Ethical Approval Not applicable.

Conflicts of Interest The authors have no conflict of interest in this research.

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