Diversifying the luminescence of phananthro-diimine ligands in zinc complexes†

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Strongly blue fluorescent 1-phenyl-2-(pyridin-2-yl)-1H-phananthro[9,10-d]imidazole (L1) is a facile block for the construction of multichromophore organic molecules, and simultaneously serves as a chelating diimine ligand. The coordination of L1 to zinc halides enhances the intraligand charge transfer and decreases the emission energy. For the iodide derivative, intra- and intermolecular heavy atom effects lead to a dual singlet–triplet emission with a temperature-dependent ratio of fluorescence and phosphorescence bands in the crystalline state. Decoration of the anthracene core with pyridyl-phananthroimidazole units (L2 and L3) changes the localization of the lowest energy electronic transitions to the former polyaromatic motif. The solid-state photophysical characteristics of L2 and L3-based compounds strongly depend on the intermolecular interactions between the constituting π-systems (phanthrene and anthracene), which are perturbed by the ZnX2 coordinated fragments. Modulation of π-stacking contacts in these molecular materials containing L2 and L3 chromophores forms a basis for dynamic optical properties, responsive to mechanical, thermal, or chemical stimuli.

Introduction

Organic platforms, which offer a range of molecular materials with versatile solid-state photophysical behavior without tedious synthetic modifications, are particularly attractive systems for the development of tunable and stimuli-responsive luminescent probes.1–8 An efficient and straightforward approach to influence the electronic structures of π-conjugated chromophores and to modulate intermolecular interactions is the employment of coordination bonding. In this respect, readily available Zn(ii) salts are considered as attractive and inexpensive modifiers of organic emitters decorated with nitrogen and oxygen donor functions. Due to the stable d10 closed shell configuration, the zinc(ii) metal center does not participate in the metal to ligand charge transfer upon electronic excitation. Therefore, the complexion of an organic motif with the Zn(ii) ion typically enhances intra-ligand fluorescence as a result of increased molecular rigidity and suppression of photoinduced electron transfer reactions. The binding of this metal can also perturb the intramolecular charge transfer (ICT) that distinctly changes the emission energy of the complex compared to that of the free ligand.9–12 Besides, the coordination-driven assembly of two or more chromophore ligands can lead to secondary interactions between the corresponding π-systems and produce aggregates with dynamic optical properties and interligand charge-transfer processes.13–15 In solution, such easily detectable responses allow for efficient luminescence sensing of the Zn(ii) ion by a variety of organic probes.16–22

In the solid state, in addition to intramolecular effects, the non-covalent intermolecular interactions, e.g. hydrogen/halogen bonding and π-stacking, govern the organization of the constituting conjugated moieties, and often play a decisive role in modulating the physical characteristics of the bulk materials.23 It is not surprising that the combination of a metal ion or of a simple MXn fragment with an extended π-molecule has a strong influence on the supramolecular arrangement of organic building blocks, and introduces supplementary intermolecular connectivity with the participation of the metal cation and X anions.24 For instance, the complexion of an amine-functionalized pyridinyl-pyrazole ligand with ZnCl2 shows an efficient alteration of the hydrogen bonding network and of the phase behavior caused by the metal halide unit.25 Tuning the π–π stacking contacts between...
the chromophores of a chiral pyrene-containing histidine by means of Zn(u) coordination has been used to switch the circularly polarized luminescence of the nanoassemblies.26 On the other hand, packing-assisted heteroleptic π-interactions between electron-poor and -rich ligands can yield solid donor-acceptor complexes with improved charge transfer properties.27 Furthermore, dense π-π stacking between aromatic linkers in Zn(u)-assembled metal-organic frameworks and coordination polymers has been identified as an important factor for enhancing long room temperature phosphorescence (RTP).28–30 In general, triplet emission rarely occurs in zinc complexes under ambient conditions because of the inefficient spin-orbit coupling (SOC) and small heavy atom effect (HAE) caused by this metal ion;31,32 the majority of the reported examples of phosphorescent materials correspond to the polymer-like species.28–30 To solve this problem, a recently proposed approach to increase the SOC, promote intersystem crossing (ISC) and populate the triplet excited state, relying on an external HAE induced by Zn-bound heavier halides or halide counterions has been applied.32,39,40 This facile strategy, which does not require modification of the organic ligand by forming covalent C–Br/I bonds, allowed RTP with quantum yields of up to 9%.29 It is noteworthy that the effect of intermolecular interactions on the photoluminescence properties of organic molecular materials is frequently manifested by remarkable mechano-, vapo- and thermo-responsive behaviors, which can be triggered or tuned as well through the coordination to various metal ions including zinc(u).41–44

In the current work, we have selected a family of easy to prepare phenanthrene-based pyridyl-imidazole ligands and their anthracene derivatives (Fig. 1), which are known to be fluorescent in solution.45 Binding these chromophores to some ZnX2 salts (X = Cl, I, OAc) has a substantial impact on the solid state photophysical behavior. A range of intermolecular contacts were found to be subtly dependent on the anions X and allowed realizing such phenomena as temperature-variable dual emission and mechanochromic luminescence, which could not be attained for the parent organic compounds.

Fig. 1 Ligands L1–L3 used in this study.

Results and discussion

Preparation of zinc complexes

Ligands L1 and L2, containing a pyridyl-imidazole coordinating function fused with a polyaromatic phenanthrene motif, were readily obtained as described earlier.45,46 L3, which comprises diethylnanthracene decorated with two diimine motifs, was synthesized in a good yield analogously to L2 (Scheme S1, see the experimental details in the ESI†).

The coordination of congener bidentate pyridyl-imidazole ligands to zinc(u) ions has been described previously for a number of polymeric and molecular complexes.47–54 Treatment of ligands L1–L3 with ZnX2 salts in dichloromethane/methanol or diethyl ether mixtures at room temperature afforded the corresponding complexes Zn(L1)X2 (1X, X = Cl 1Cl, I 1I, OAc 1OAc), Zn(L2)X2 (2X, X = Cl 2Cl, I 2I, OAc 2OAc) and Zn3(L3)(OAc)4 (3OAc), which were isolated as stable crystalline solids (75–97%), Scheme 1. The halide congeners of 3OAc are very poorly soluble that prevented their purification and characterization. The 1H NMR spectra of the halide complexes measured in chloroform show well-resolved patterns, which indicate that these species retain the proposed structures in solution (Fig. S1–S3†).

The acetate compounds, particularly 2OAc and 3OAc, show concentration dependent behavior in solution, which is tentatively attributed to the reversible dissociation of Zn(OAc)2 motifs. Similar coordination–decoordination has been observed for a terpyridine-derived complex.9 Thus, in the case of 2OAc, lowering the concentration ultimately allows the identification of the signals of the free ligand (Fig. S2†) that confirms the hypothesis. The presence of two metal centers in 3OAc essentially leads to somewhat different dynamics and explains the lack of ligand L3 in a solution of the complex. It should be mentioned that multiple recrystallizations of 3OAc

Scheme 1. Synthesis of the ZnX2 complexes with L1–L3 ligands (reaction conditions: methanol or diethyl ether/dichloromethane, 2 h, 298 K).
result in the appearance of substantial amounts of uncoordinated L3, which is in line with the limited stability of zinc acetate compounds 1-3OAc in solution.

**Photophysical studies in solution**

The optical properties of L1 and L2 were described in an earlier publication.45 The lowest energy absorption and emission bands of L1 are assigned to a mixture of πphen → π*phen/π*py transitions. The coordination of zinc halide units to L1 causes a bathochromic shift of bands in both 1Cl and 1I (Table 1 and Fig. 2), which is in accordance with the reported effect of zinc complexation.55-58 The metal perturbation evidently leads to an appreciable πphen → π*py intraligand charge transfer (ILCT) character and stabilization of the π*py orbitals (LUMO) as confirmed by TD-DFT analysis (see the predicted calculated wavelengths of L1Cl to 0.02 (1I).

Under oxygen-free conditions, a rather weak lower energy band (λem = 518, 555 nm) can be detected for 1I (Fig. 2, the decay profile is shown in Fig. S5†). A long lifetime of 2.7 µs suggests that the signal arises from the triplet manifold with substantial ligand-centered nature (i.e. ^3π*), as pointed by discernible vibronic progression (ca. 1290 cm⁻¹).

The decrease of the fluorescence intensity for 1I and the appearance of the triplet emission indicate that a rather fast ISC (S1 → T1) takes place resulting in the population of the triplet excited state. This process is likely facilitated by the internal heavy atom effect caused by two iodine ligands. According to the population analysis, the HOMO and the LUMO of 1I (Fig. 3), which constitute 98% of the S0 → T1 tran-

**Table 1** Photophysical properties of ligands L1–L3 and their zinc complexes in solution (1,2-dichloroethane, 298 K)

| Ligand | λabs, nm (ε, 10⁴ M⁻¹ cm⁻¹) | λem, nm | Φ | τns | kobs, s⁻¹ | kν, s⁻¹ |
|--------|---------------------------|--------|---|-----|-----------|--------|
| L1Cl   | 261 (10.0), 316 (3.0), 330 (3.3), 346 (2.5), 362 (2.5) | 370, 388 | 0.37 | 1.9 | 1.9 × 10⁸ | 3.3 × 10⁸ |
| L1I    | 261 (6.8), 367 (2.6), 379 (2.6) | 371, 434 | 0.45 | 2.3 | 2.0 × 10⁸ | 2.4 × 10⁸ |
| L2Cl   | 260 (7.6), 369 (2.8), 382 (2.8) | 371, 403 (518), 555 | 0.02 | <1@433 nm | (2700@560 nm) | 2.6 × 10⁸ | 2.0 × 10⁸ |
| L2I    | 262 (6.8), 322 (2.2), 347 (2.1), 363 (2.4) | 372, 390, 407 | 0.57 | 2.2 | 2.0 × 10⁸ | 1.1 × 10⁸ |
| L3Cl   | 254 (2.4), 292 (5.2), 306 (6.4), 330 (3.4), 347 (3.0), 363 (3.7), 402 (3.8), 425 (3.6) | 433, 459, 486 | 0.65 | 3.3 | 2.0 × 10⁸ | 1.1 × 10⁸ |
| L3I    | 262 (13.3), 303 (2.9), 384 (4.1), 429 (2.5) | 442, 465 | 0.40 | 6.4 | 6.3 × 10⁷ | 9.4 × 10⁷ |
| L4Cl   | 263 (12.3), 303 (2.9), 385 (3.9), 429 (2.5) | 442, 465 | 0.20 | 5.4 | 3.7 × 10⁷ | 1.5 × 10⁷ |
| L4I    | 263 (11.6), 306 (4.3), 364 (2.8), 402 (2.7), 426 (2.5) | 436, 460, 487 | 0.58 | 3.6 | 1.6 × 10⁸ | 1.2 × 10⁸ |
| L3Cl   | 262 (14.1), 274 (13.4), 319 (8.2), 346 (3.4), 363 (3.5), 447 (4.6), 473 (5.0) | 486, 515, 550sh | 0.60 | 2.6 | 2.3 × 10⁸ | 1.5 × 10⁸ |
| L3I    | 262 (17.3), 274 (15.7), 319 (8.0), 345 (3.5), 363 (3.8), 447 (4.8), 473 (5.2) | 485, 516, 550sh | 0.65 | 2.6 | 2.5 × 10⁸ | 1.3 × 10⁸ |

λabs: 365 nm for 1Cl, L3 and 3OAc and λabs: 330 nm for other compounds. ^kν values were estimated by Φ/νobs. †kν values were estimated by (1 – Φ)/νobs. *Emission data in dichloromethane from ref. 45. †Data obtained under deaerated conditions. ‡In aerated solution. †sh stands for shoulder.
Symmetrical substitution of anthracene in L3 results in some extension of the conjugated \( \pi \)-system, and therefore decreases the optical band gap \( \Delta E_{\text{opt}} \) (HOMO–LUMO) to 2.9 eV compared to that of L2 (3.3 eV). Overall, the fluorescence spectra of these ligands (Fig. 2 and 5) resemble those of the corresponding phenylethynyl anthracenes.\(^{63}\) Due to the lack of electronic communication of the emissive motif with the metal-coordinating parts of the ligand, the emission bands of the ligands L2 and L3 and respective zinc complexes 2X, 3OAc (Fig. 2 and 5) are very similar and reveal the clearly resolved vibrational structure arising from their \( \pi^* \) character (Table S1;\(^{61}\) Fig. 4, S6 and S7). The effect of metal binding to L2 and L3 on the photophysics is mainly seen in a decrease in the quantum yield of halides, \( \Phi_{\text{em}} \text{L2} > 2\text{Cl} > 2\text{I} \), which probably suggests some excitation energy transfer to the predominantly dark triplet state of the phenanthroimidazole fragment.

### Structural and photophysical studies in the solid state

The pertinent luminescence data are listed in Table 2. The emission properties of the titled complexes in the solid state substantially depend on the molecular packing, and therefore their discussion is carried out together with systematic crystallographic and photophysical parameters. The low-temperature solid-state spectra of these ligands (Fig. 2 and 5) are very similar and reveal the clearly resolved vibrational structure arising from their \( \pi^* \) character (Table S1;\(^{61}\) Fig. 4, S6 and S7). The effect of metal binding to L2 and L3 in the solid state is mainly seen in a decrease in the quantum yield of halides, \( \Phi_{\text{em}} \text{L2} > 2\text{Cl} > 2\text{I} \), which probably suggests some excitation energy transfer to the predominantly dark triplet state of the phenanthroimidazole fragment.

#### Table 2 Photophysical properties of ligands L1–L3 and their zinc complexes in the solid state (298 K)

|            | \( \lambda_{\text{em}} \text{ nm} \) | \( \Phi \)  | \( \tau_i \text{ ns}^a \) | \( k_{\text{nr}}b^a \text{s}^{-1} \) | \( k_{\text{nr}}c^a \text{s}^{-1} \) |
|------------|-------------------------------|--------|-----------------|-----------------|-----------------|
| L1         | 413                           | 0.12   | 3.0             | \( 4.0 \times 10^7 \) | \( 2.9 \times 10^8 \) |
| 1Cl_a      | 460                           | 0.28   | 2.7             | \( 1.0 \times 10^8 \) | \( 2.7 \times 10^8 \) |
| 1Cl_b      | 464(sh), 473                   | 0.19   | 1.7             | \( 1.1 \times 10^8 \) | \( 4.8 \times 10^8 \) |
| 1I_a       | 469                           | 0.01   | 0.5             | \( 2.0 \times 10^8 \) | \( 2.0 \times 10^8 \) |
| 1I_b       | 470, 554, 596                  | 0.03   | 1.0, 10^5      | \( 7.0 \times 10^7 \) | \( 4.3 \times 10^8 \) |
| 10Ac       | 478                           | 0.14   | 2.0             | \( 1.0 \times 10^8 \) | \( 3.3 \times 10^8 \) |
| L2         | 497                           | 0.03   | 2.9             | \( 1.9 \times 10^7 \) | \( 6.1 \times 10^8 \) |
| 2Cl        | 471                           | 0.03   | 1.6             | \( 1.9 \times 10^7 \) | \( 6.1 \times 10^8 \) |
| 2I         | 506(sh), 598                   | 0.06   | 1.3, 3.6       | \( 1.3 \times 10^7 \) | \( 6.1 \times 10^8 \) |
| 2OAc       | 497                           | 0.02   | 1.6             | \( 1.3 \times 10^7 \) | \( 6.1 \times 10^8 \) |
| L3_y       | 543                           | 0.04   | 2.6             | \( 1.5 \times 10^7 \) | \( 3.7 \times 10^8 \) |
| L3_r (red) | 597                           | 0.03   | 2.3             | \( 1.3 \times 10^7 \) | \( 4.2 \times 10^8 \) |
| 3OAc_y     | 562                           | 0.03   | 3.5             | \( 8.6 \times 10^6 \) | \( 2.8 \times 10^8 \) |
| 3OAc_r     | 611                           | 0.06   | 3.4             | \( 8.6 \times 10^6 \) | \( 2.8 \times 10^8 \) |

\(^a\) Average emission lifetime for the two exponential decay \( \tau_{\text{av}} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1^2 + A_2\tau_2^2) \), \( A_i \) are pre-exponential factors. \(^b\) \( k_i \) values were estimated by \( \Phi/k_{\text{nr}} \). \(^c\) \( k_{\text{nr}} \) values were estimated by \( (1 - \Phi)/k_{\text{nr}} \).
Crystalline species demonstrate a rather minor variation (adjacent molecules. However, the emission maxima of these which involve both polyaromatic and the pyridine motifs of solvate of the iodide complex 1I_a (Fig. S9) show π–π stacking interactions between the phenanthrene systems (Fig. S9†).

The acetate 1OAc (Fig. S10†) and the dichloromethane solvate of the iodide complex 1I_a (Fig. 7) show π–π contacts, which involve both polyaromatic and the pyridine motifs of adjacent molecules. However, the emission maxima of these crystalline species demonstrate a rather minor variation (λ_em = 460–478 nm, Fig. 6) indicating that stacking in this case has a moderate influence on the properties of the excited state. Analogously to the solution behavior, the luminescence of 1X in the solid form is manifested by broad structureless bands, which are observed at lower energies than those of the parent L1. The excitation spectra of L1 and 1X (Fig. S11†) follow the same trend that complies with the change in the nature of the S1 state of complexes and the substantial ILCT character of the emission of 1X. The chloride and acetate compounds 1X are somewhat more efficient fluorophores (Φ_em = 0.14–0.28) than the free ligand primarily due to the increased radiative decay rate of ca. 1.0 × 10^8 s^{-1} (Table 2). As in solution, the iodide 1I_b in the solid state (in both forms 1I_a and 1I_b) exhibits the lowest quantum yield due to the ISC (S1 → T_n) transition to the dark triplet state, similar to zinc halide compounds with pyridylimidazo-pyridine ligands.55 While 1I_a does not show room temperature phosphorescence, the solvent-free modification to 1I_b is dually emissive (Fig. 6). It demonstrates a dominating high energy fluorescence band (λ_em = 470 nm), which is accompanied by a low energy structured signal (λ_em = 554, 596; total Φ_em = 0.03) with a long observed lifetime of ca. 100 μs. In contrast to 1I_a, no appreciable π–π interactions are seen in 1I_b. Instead, 1I_b forms short intermolecular contacts I⋯π (ca. 3.5 Å, Fig. 7) between the iodide ligand and the imidazole ring...
(cf. 4.121 Å for analogous separation in 11_a). This unique arrangement presumably accounts for the enhancement of the external HAE in 11_b that causes larger SOC and results in detectable intraligand triplet emission under ambient conditions. The importance of the HAE and of close halide⋯chromophore contacts in promoting SOC has been recently shown for zinc halide coordination polymers prepared via a 1,3,5-tris[(1-imidazolyl)]benzene luminescent linker.

Decreasing the temperature has a drastic influence on the ratio of fluorescence and phosphorescence intensities of form 11_b (Fig. 8A and Table S7†). Upon cooling the crystals of 11_b, the low energy band shows a drastic growth that produces white-orange luminescence, whereas the observed lifetime of the red shifted band increases from ca. 100 μs at 298 K to 2.2 ms at 77 K. Taking into account that SOC induced by the HAE is proportional in the first approximation to \( Z^4/r^3 \) (\( Z \) is the atomic number and \( r \) is the distance between the chromophore and the heavy atom), and then the rate of ISC, \( k_{isc} \propto |\Psi_{T1}\rangle \langle HSO|\Psi_{S1}|^2/(\Delta E_{S1-T1})^2, \) is related to the distance as \( 1/r^6. \) This implies that the probability of populating the T1 state is highly sensitive to intermolecular separation for 11_b assuming the external HAE.

To assess the correlation of the emission with the structural parameters and temperature, we performed variable-temperature XRD studies. Indeed, the intermolecular distance I⋯\pi_{imi} is nearly linearly dependent on the temperature and decreases from 3.572 Å at 295 K to 3.499 Å at 150 K (Fig. 8B, Table S7†) that could be one of the decisive factors that determines the increase of phosphorescence vs. fluorescence. In addition to the triplet luminescence, which is uncommon for zinc complexes,13,31,65,66 11_b represents an interesting example of a reversibly responsive material, the emission color of which (Fig. 8C) is regulated by the temperature-dependent ratio of the singlet and triplet radiative decays.

Form 11_a also exhibits luminescence thermochromism (Fig. S12†), although in a less pronounced manner compared to 11_b. In the absence of short I⋯\pi contacts, a notable increase of the phosphorescence band of 11_a starts at around 150 K that can be attributed to the rigidification of the structure and moderate intra- and intermolecular heavy atom effects.

**L2 and 2X series.** The emission of the solid ligand L2 (\( \lambda_{em} = 497 \) nm, Fig. 9A) is unstructured and is found at a longer wavelength in comparison with that in solution (\( \lambda_{em} = 433 \) nm, Fig. 8A).
Fig. 2). Substantial quenching of luminescence in the solid state (ca. 20-fold decrease vs. solution, Table 1) and the decrease in energy likely arise from certain π-interactions between the chromophore anthracene fragments, however, the assignment to either perturbed monomer or excimer emission is ambiguous on the basis of the available data.67,68 The quantum yield, observed lifetimes, and the excitation and emission profiles of L2 and 20Ac are very similar (Fig. 9 and S13†), whereas the fluorescence maxima nearly coincide that suggests resembling resemblance in the packing and the nature of the excited states. The hypsochromic shift of the fluorescence band of the crystalline chloride complex 2Cl (λem = 471 nm, Fig. 9A) confirms the monomer anthracene emission. Indeed, the structure of 2Cl (Fig. S14†) confirms that the anthracene π-system is not involved in appreciable stacking interactions, which are found between the phenanthrene fragments only. Mechanical grinding of the pristine sample 2Cl produces an amorphous material exhibiting green-yellow luminescence (λem = 532 nm, Fig. 9B and Table S8†). Together with the visibly changed excitation spectrum (Fig. S13†), it points to the alteration of molecular packing, which conceivably results in the emergence of π-interactions between the anthracene chromophores. On the other hand, grinding of 20Ac has a little influence on the fluorescence spectrum (Fig. S15†).

Unlike 2Cl and 20Ac, the crystalline iodide congener 2I is a dual emitter with the dominating band with the maximum at 598 nm (Fig. 9A) and the observed lifetime of 3.6 ns. Such a significant red shift is not typical of anthracene excimer fluorescence.69,70 The crystal structure of 2I shows short π–π contacts between the emissive anthracene and phenanthrene fragments (Fig. 10) that makes the formation of an exciplex or intermolecular charge transfer (anthracene → phenanthroimidazole) possible. The excitation spectrum of 2I monitored at 620 nm clearly differs from those of other 2X species and shows an intense red shifted band (Fig. S13†) that assumes ground state aggregation. The minor high energy band in the emission of 2I (λem = 506 nm) plausibly arises from the locally excited state, i.e. corresponding to the monomer anthracene luminescence. This signal might originate for instance from the surface/peripheral molecules, which experience less intermolecular interactions.71,72 The impact of mechanical stimulus on the emission pattern of 2I is rather moderate and results in the growth of some blue shifted bands (Fig. 9C), evidently due to the high stability of the crystalline packing mode. However, the fluorescence of a film-like sample prepared by fast evaporation of a dichloromethane solution of 2I is essentially switched mainly to the monomer origin with the maximum at 494 nm and a distinguishable vibrational structure (ca. 1160 cm⁻¹) due to the lack of intermolecular interactions. The excitation spectrum of the dropcast sample 2I is similar to those of 20Ac and ground 2Cl, and therefore supports the disruption of charge-transfer anthracene–phenanthrene stacking in the amorphous state.

L3 and complex 30Ac. Depending on the conditions, ligand L3 and the zinc acetate derivative 30Ac can be isolated by at least two modifications (see the ESI), which show distinctly different luminescence characteristics (Fig. 11). The minor yellow crystalline forms of L3_y and 30Ac_y were structurally characterized (Fig. S16† and Fig. 12).

Although these single crystals do not represent the bulk yellow modifications L3_y/30Ac_y, the photophysics of which was analyzed, similar colours of the samples suggest that they have similar arrangements in the solid. According to the XRD data, the diethynyl anthracene fragments of the chromophore do not show appreciable stacking interactions, and therefore the observed yellow fluorescence (λem = 543/562 nm, Φem = 0.04/0.03 for L3_y/30Ac_y) presumably corresponds to the monomer emission, broadened and red shifted with respect to the solution spectrum (Fig. 5).

Although we could not obtain crystals of L3_r/30Ac_r suitable for structural analysis, the colours of these solids and of their luminescence (λem = 597/611 nm, Φem = 0.03/0.06 for L3_r/30Ac_r) propound aggregation with the involvement of the emissive anthracene centers, reminiscent of the crystalline 9,10-bis[phenylethynyl]anthracene (BPEA).73 The emissions of both forms of the complex are visibly red shifted compared to...
those of the corresponding L3_y/r forms of the ligand (Fig. 11A). The lowest energy maxima of the excitation spectra for the yellow and orange-red modifications vary by more than 60 nm (Fig. S17†), and thus corroborate that different molecular packings generate the excited states operating in these materials.

Ligand L3 demonstrates distinct stimuli-responsive behaviour. Mechanical grinding of yellow L3_y produces a metastable orange material (o1, λem = 575 nm). Brief heating (up to ca. 300 °C) or exposure to vapors of diethyl ether further transforms this solid into the red form, the emission of which (λem = 598 nm) is nearly identical to that of the independently prepared L3_r (Fig. 11B). Grinding the red form leads to another metastable orange modification (o2, λem = 564 nm), the process is also reversible thermally by means of vapors. The transitions between different forms apparently result from the perturbation of intermolecular interactions, which involved the anthracene chromophore.

Albeit phenanthroimidazole fragments in L3 and 3OAc are not expected to contribute to the frontier orbitals according to the theoretical studies (Fig. S7†), apparently, they influence the intermolecular organization and mechano-/vapo-responsive behaviour. The coordinating ability of the pendant groups can be used to tune these features as the binding of zinc acetate e.g. bathochromically shifts the emission of both phases from 543/597 nm (L3) to 562/611 nm (3OAc, Table 2). The photophysical properties of the yellow and orange-red forms of L3/3OAc remind those of a film (yellow) and crystals (orange-red) of BPEA.72,74 On the other hand, the fluorescence mechanochromism of some functionalized BPEA-s is clearly less expressed.75,76

Conclusions

In this study, we have analysed the photophysical behaviour of readily available fluorophores L1–L3, which comprise a pyridyl-imidazole coordinating function fused with a polyaromatic phenanthrene motif, and their zinc(II) complexes 1X–3X derived from simple ZnX2 salts (X = Cl, I, OAc). In solution, the optical properties of organic emitters and the corresponding metal-containing species are governed by the intraligand charge transfer and ππ* electronic transitions of the singlet parentage, localized either on the phenanthrene-diimine system (L1 and 1X) or within the alkynyl-anthracene chromophore fragment (L2 and L3-based compounds). However, the ZnX2 units cause little perturbation to the intraligand fluorescence of L2 and L3 in fluid medium, and coordination of zinc halide units to L1 red shifts the lowest energy absorption and emission bands in 1Cl and 1I due to the enhanced πphen → π*py CT. In the case of 1I, the intramolecular heavy atom effect associated with iodide ligands facilitates ISC resulting in a significant decrease in the fluorescence intensity.
and in the phosphorescence emission, seldom observed for zinc coordination complexes in solution.

The investigation of luminescence properties in the solid state was supported by extensive structural characterization of the title compounds. Systematic crystallographic studies highlight a strong impact of ZnX₂ groups on non-covalent intermolecular interactions, and as a consequence, on the optical features of these materials. In particular, the iodide complex 11 demonstrates packing-dependent dual (singlet–triplet) emission, which has been correlated with short intermolecular π⋯π contacts. In turn, due to the temperature variability of this distance and the alteration of the phosphorescence vs. fluorescence ratio, the solvent-free crystals of 11 exhibit a distinct emission color change from blue to yellow-orange in a temperature range of 150–300 K.

Switching the emissive center to the anthracene moiety in L2 and L3-based species provides more possibilities for responsive properties based on the ground state π–π interactions (anthracene–phenanthrene and anthracene–anthracene). It is noteworthy that L3 and 30AE exist in several forms exhibiting different fluorescence performances (λ_em alters from 543 to 597 nm for L3), which can be interconverted by means of various stimuli (mechanical and thermal treatment and exposure to a solvent). Overall, accessible preparation of organic chromophores with coordinating ability and their combination with optically innocent metal ions such as zinc offer a wide range of possibilities for the development of easy to synthesize molecular materials with diverse photophysical functionalities.

Author contributions

D. T. and K. S. K. contributed equally and performed the synthesis, and structural and NMR spectroscopic characterization. T. E. and P. H. were responsible for computational analysis. N.K. carried out PXRD measurements. K. S. K., J. R. S. and A. S. M. performed the photophysical studies. S. P. T., E. V. G. and I. O. K. planned the research.

Conflicts of interest

There are no conflicts to declare.

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