Tetraguanidino-functionalized phenazine and fluorene dyes: synthesis, optical properties and metal coordination†

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In this work the first phenazine derivatives with guanidino substituents were prepared and their structural and electronic properties studied in detail. The guanidino groups decrease the HOMO–LUMO gap, massively increase the quantum yield for fluorescence and offer sites for metal coordination. The yellow-orange colored 2,3,7,8-tetraguanidino-substituted phenazine shows intense fluorescence. The wavelength of the fluorescence signal is strongly solvent dependent, covering a region from 515 nm in Et2O solution (with a record quantum yield of 0.39 in Et2O) to 640 nm in water. 2,3-Bisguanidino-substituted phenazine is less fluorescent (maximum quantum yield of 0.17 in THF), but exhibits extremely large Stokes shifts. In contrast, guanidino-functionalized fluorenes emit only very weakly. Subsequently, the influence of coordination on the electronic properties and especially the fluorescence of the phenazine system was analysed. Coordination first takes place at the guanidino groups, and leads to a blue shift of the luminescence signal as well as a massive decrease of the luminescence lifetime. Luminescence is almost quenched completely upon Cu¹ coordination. On the other hand, in the case of Zn⁰ coordination the fluorescence signal remains strong (quantum yield of 0.36 in CH3CN). In the case of strong zinc Lewis acids, an excess of metal compound leads to additional coordination at the phenazine N atoms. This is accompanied by significant red-shifts of the lowest-energy transition in the absorption and fluorescence spectra. Pentanuclear complexes with two phenazine units were isolated and structurally characterized, and further aggregation leads to chain polymers.

Introduction

Amino-substituted phenazines and fluorenes are important dyes. Hence the phenazine derivative mauveine (Perkin’s dye, which actually was shown to be a mixture of several compounds which differ in the number of methyl groups) was the first commercialized synthetic dye.† Although its last commercial use (coloring of British stamps) ended in 1901, mauveine was of great importance for the development of the modern chemical industry.2 Other known phenazine dyes include safranin and Neutral red. All these compounds feature amino substituents. The amino functions increase the electron density on the aromatic system and the quantum yield of fluorescence by suppressing nonradiative relaxation processes. There are also other applications that make phenazines attractive for modern chemistry, spanning from organic electronics (phenazines have been integrated in solar cell† and organic light emitting diode (OLED)⁴ devices) to sensors (e.g. pH⁵ or metal sensing⁶,⁷ and pharmaceutical purposes (especially DNA intercalation). Fluorenes are attractive building blocks in polymers, and polyfluorenes are electrically conductive and electroluminescent.⁸ Hence fluorenes and polymers including fluorene units are intensively applied in OLED devices.⁹ Fluorene and triphenylene derivatives have been integrated into porous covalent organic frameworks with distinct optical and electronic properties.¹⁰,¹¹

The influence of metal coordination on the optical properties of fluorophores was intensively studied in the past.¹²,¹³ Photoluminescent sensors based on the photo-induced electron transfer (PET) mechanism were built by linking fluorophors (through a spacer) to ionophores, which are responsible for metal coordination.¹⁴,¹⁵ In its bound state, the ionophore usually forms a chelating complex with the metal ion. For
example, for zinc sensing, the ionophore often contains pyridyl groups. In classical PET probes, the HOMO energy of the free (uncoordinated) ionophore (e.g. “formed” by N donor atom lone pairs) is slightly higher than the relevant orbital energy of the fluorophore, so that intramolecular electron transfer (through the spacer) upon photoexcitation of the fluorophore leads to fluorescence quenching. In the bound (metal coordinated) ionophore the HOMO energy is then drawn down below the fluorophore orbital energy, leading to strong fluorescence. This is termed CHEF (chelation enhanced fluorescence) effect. On the other hand, coordination of transition metals with unpaired electrons such as Cu\(^{2+}\) (like coordination of heavy metal ions) generally leads to fluorescence quenching.

In this work we report the first phenazine and fluorene derivatives with guanidine substituents, namely 2,3,7,8-tetraamino-phenazine (1) and 2,3,6,7-tetrakis(tetramethylguanidino)fluorene (2). The guanidine groups, which outperform in several aspects the amino groups, fulfill several tasks. They massively increase the quantum yield for fluorescence in the phenazine derivative. In addition, they increase the solubility in organic solvents and also in aqueous solutions, and prohibit, at least to some extent, aggregation processes which could lead to quenching of the fluorescence. Many previous experiments with guanidine-substituted aromatic compounds by our group showed that the guanidine groups increase significantly the HOMO energy and decrease the HOMO–LUMO gap. Last but not least, they offer sites for metal coordination. In this work, the coordination chemistry and optical properties (absorption and emission spectra) will be addressed in particular.

Neutral guanidines as well as guanidinates were shown to be excellent ligands, which were applied in coordination chemistry for manifold purposes. Cu\(^{1+}\) complexes of tripodal tris(2-guanidinylethyl)amine ligands were used for the preparation of end-on bonded superoxo-complexes which exhibit a rich chemistry. Other guanidine ligands were used as catalysts, e.g. in lactide polymerization or Heck-type reactions. Generally only the imino-N atom of the guanidine binds to the metal, since the lone-pairs on the amino N atoms are engaged in π-interactions. However, in exceptional cases the amino group also binds to the metal, leading to additional hemilabile metal–ligand bonding which is of interest for catalytic applications. A detailed analysis of the guanidine-metal bonding on the basis of a experimental charge-density study revealed σ-as well as π-bonding contributions, in line with the observed elongation of the C–N imino bond upon coordination. Our group recently established guanidino-functionalized aromatic compounds (GFAs) as a new class of strong organic electron donors. The Lewis-structures of two representatives, namely 1,2,4,5-tetrakis(tetramethylguanidino)benzene, and 2,3,5,6-tetrakis(tetramethylguanidino)pyridine, are shown in Scheme 1. According to cyclic voltammetric (CV) experiments, both compounds exhibit a similar electron-donor capacity with an \(E_{1/2}\) value (in CH\(_2\)Cl\(_2\)) of \(-0.76\) V versus Fe/Fe\(^{3+}\) (Fc = ferrocene) for two-electron oxidation. On the other hand, 4 but not 3 could be used in photochemical reductive C–C coupling reactions. We have analysed in some detail the effect of alkylation of the pyridine N atom on the electronic properties of 4. Alkylation leads to a red-shift of the lowest-energy electronic transition (LUMO ← HOMO excitation). We show in this work that coordination at the N atoms of the phenazine core of compound 1 also changes the electronic properties.

**Results and discussion**

**Synthesis and structural characterization**

The new GFA 1 was synthesized in a three step reaction starting with 1,2,4,5-tetraamino-benzene. Heating an aqueous solution of 1,2,4,5-tetraamino-benzene·4HCl in the presence of NaOAc (sodium acetate) and under a stream of compressed air gave deep purple-colored 2,3,7,8-tetraamino-phenazine-tri-
hydrochloride, a reaction which was already previously described. Then this compound was reacted with activated tetramethyl-urea (the “Vilsmeier” salt 2-chloro-1,1,3,3-tetramethylformamidinium chloride, [ClC(NMe₂)₂]Cl) to yield 1 in the form of an orange-colored solid. Deeply orange-colored crystals suitable for a single-crystal X-ray diffraction analysis were obtained from Et₂O solutions. We also synthesized the corresponding bisguanidine 1,2-bis(tetramethylguanidino)phenazine, 5 (see Scheme 3), from 1,2-diamino-phenazine (also an orange-colored solid at ambient conditions). The amino precursor to compound 2, namely 2,3,6,7-tetramino-fluorene-tetrahydrochloride, was synthesized according to the literature (with minor modifications, see Experimental details) starting with 2,7-dinitrofluorene (see Scheme 2). Guanidinylation was again achieved with activated tetramethyl-urea in the presence of NEt₃. The structures of compounds 1, 2 and 5, as derived from single-crystal X-ray diffraction, are visualized in Fig. 1. The imino C=⁻N bond distances adopt characteristic average values of 1.300 Å in 1, 1.293 Å in 2 and 1.317 Å in 5. These values generally increase upon metal coordination (see below). According to ¹H NMR studies the guanidino groups are highly flexible, so that at room temperature all 48 methyl protons in 1 and 2 and all 24 methyl protons of 5 exhibit the same chemical shift.

We also measured CV curves to study the redox activity of the new compounds. Fig. S1 (see ESI†) displays the CV curve for compound 1. It contains four oxidation waves, centered at −0.12, 0.08, 0.38 and 0.63 V vs. Fe/Fc⁺ (Fc = ferrocene), showing that the compound could be oxidized at a lower potential than ferrocene. Three reduction waves of different intensity appear at −0.39, −0.23 and 0.24 V. The curve shows that the guanidino groups indeed turn phenazine into an electron donor. On the other hand, they clearly indicate a non-reversible redox behaviour, in contrast to the fully reversible oxidation processes for compounds 3 and 4.²⁶,²⁷ On the basis of this result, the further discussion focuses on the optical properties rather than the redox-chemistry.
Next we studied the optical properties of the two new GFA compounds 1 and 2 and of bisguanidine 5. Compound 1 turned out to be soluble in several organic solvents and also water, yielding yellow-orange colored solutions. The electronic absorption spectrum of an aqueous solution of 1 is shown in Fig. 2. It contains strong bands at 229, 300 (with a shoulder at 311), 432 and 484 nm. Due to the high basicity of guanidines, a large portion of the molecules is protonated. Addition of HCl to the solution leads to a decrease of the 484 nm band, and an increase of the 432 nm band. Upon addition of 12 equivalents of HCl the 484 nm band is extinguished (see Fig. 2a). On the other hand, addition of NaOH leads to the increase of the band at higher wavelength (the maximum shifts slightly from 484 nm to 493 nm) at the expense of the 432 nm band (Fig. 2b). On the basis of these results we assign the 484 nm band to the unprotonated compound, and the band at 432 nm to the protonated species. The corresponding emission spectra are shown in Fig. 3. Without acid or base addition, the fluorescence quantum yield in water is 0.02. HCl addition leads to fluorescence quenching, and NaOH addition to a massive increase of the fluorescence signal. Hence only the unprotonated, but not the protonated species shows fluorescence. The
emission maximum after addition of 10 eq. of HCl is reached at $\lambda_{\text{max}} = 634$ nm, leading to a substantial Stokes shift of 4510 cm$^{-1}$. Since the compound offers two different sites for protonation (the N atoms in the phenazine heterocycle and the imino N atom of the guanidino group), we studied protonation in some more detail. Addition of an ammonium salt (NH$_4$)X (X = PF$_6$ or BF$_4$) led to twofold protonation. Crystals of the salt $[\text{1H}^2\text{H}]$BF$_4$$_2$ were grown and the structural elucidation showed protonation exclusively at the guanidino groups (see Fig. S2 in the ESI†). On the other hand, quantum chemical calculations (B3LYP/6-311G**) predict a preference for the proton to bind to the N atom of the heterocycle. Hence the Gibbs free energy change (at 298 K, 1 bar) for tautomerization of $\text{1H}^+$ in the gas-phase according to Scheme 4 was calculated to be $-23$ kJ mol$^{-1}$. Similar results were previously obtained for 2,3,5,6-tetrakis(tetramethylguanidino)pyridine, for which protonation at the pyridine N atom is favoured by $-24$ kJ mol$^{-1}$ ($\Delta G$ value at 298 K, 1 bar).$^{27}$

Subsequently we studied the influence of different solvents on the absorption and emission spectra. In Fig. 4a, the light emitted from several solutions, excited with UV light, is visualized. It can be seen that the emission intensity and also the wavelength vary. The intensity is particularly high in Et$_2$O, for which we determined a quantum yield of fluorescence of 0.39. To the best of our knowledge, this is the highest quantum yield measured for a molecular simple phenazine derivative. For comparison, Safranine O exhibits a quantum yield of 0.06 in H$_2$O and 0.29 in EtOH,$^{33}$ and dipyrido[3,2-\text{a}\text{2}',3'\text{c}]phenazine of 0.009 in CH$_2$Cl$_2$.$^{34}$ Fig. 4b shows the absorption and emission spectra (excited at 480 nm) of 1 in CH$_3$CN and Et$_2$O. The emission maximum is reached at 515 nm, being thus strongly blue-shifted by more than 100 nm with respect to aqueous solution. The absorption maximum for the corresponding electronic transition is located at 484 nm, at the same position than in H$_2$O, and thus the Stokes shift in Et$_2$O solution (2130 cm$^{-1}$) is much smaller than in aqueous solutions of the compound. For comparison, Fig. 4b also includes the UV/Vis spectrum of unsubstituted phenazine in CH$_3$CN. The decrease of the HOMO–LUMO gap by the guanidino groups manifests itself in a massive red-shift of the lowest-energy band (located around 363 nm in phenazine, but 484 nm in 1).

Table 1 gives an overview over the wavenumbers for absorption and emission and the Stokes shifts in several solvents.

At this stage, it appeared to us attractive to compare the optical properties of compound 1 bearing four guanidino...
groups with that of compound 5 bearing only two guanidino groups. Fig. S3 in the ESI† shows photos of the emission from solutions of 5 in different solvents, excited with UV light, and some representative absorption and emission spectra. Especially intense emission signals were observed in Et2O and THF. However, the quantum yields of 0.11 determined in Et2O and 0.17 in THF are smaller than for 1. The lowest-energetic band in the absorption spectrum of 5 (at 393 nm in CH3CN, Fig. S3 in the ESI† shows photos of the emission from solutions of 5 in different solvents, excited with UV light, and some representative absorption and emission spectra. Especially intense emission signals were observed in Et2O and THF. However, the quantum yields of 0.11 determined in Et2O and 0.17 in THF are smaller than for 1. The lowest-energetic band in the absorption spectrum of 5 (at 393 nm in CH3CN,

**Fig. 4** (a) Photos showing the emission of solutions of compound 1 in different organic solvents. (b) Electronic absorption and emission spectra for solutions of compound 1 in CH3CN and in Et2O solution. (c) Calculated HOMO and LUMO energies (B3LYP/6-311G**) of 1 relative to unsubstituted phenazine.
Interestingly, the average lifetimes are nearly independent of the excitation wavelength in CH$_3$CN.

\[ \text{Stokes shift/cm}^{-1} \text{ for } 1, [\text{I(ZnCl}_2\text{)}], 5 \text{ and } [\text{I(ZnCl}_2\text{)}] \text{ and different solvents} \]

| Compound | Solvent    | $\lambda_{\text{max, abs}}$ (nm) | $\lambda_{\text{max, em}}$ (nm) | Stokes shift$^1$ (cm$^{-1}$) |
|----------|------------|---------------------------------|---------------------------------|-----------------------------|
| 1        | Et$_2$O    | 302, 444, 464                   | 515                             | 2130                        |
|          | CH$_2$Cl$_2$ | 311, 487                       | 546                             | 2220                        |
|          | CH$_3$CN   | 221, 309, 484                   | 568                             | 3060                        |
|          | H$_2$O     | 229, 300, 311s, 432, 484        | 640                             | 5040                        |
|          | pH $\gg$ 7 | 493$^a$                        | 634                             | 4510                        |
|          | pH $\ll$ 7 | 432$^a$                        | 583                             | 6000                        |
| [1(ZnCl$_2\text{)}]  | CH$_3$CN   | 228, 316, 458, 484              | 506                             | 898                         |
|          | CH$_2$Cl$_2$ | 228, 319, 459, 486              | 512                             | 1050                        |
| [(1$_2$ZnCl$_2\text{)}]  | CH$_2$Cl$_2$ | 581$^a$                        | 599                             | 517                         |
| 5        | Et$_2$O    | 277, 433                       | 568                             | 5490                        |
|          | CH$_3$CN   | 233, 276, 393                   | 599                             | 8750                        |
|          | THF        | 227, 278, 435                   | 588                             | 5980                        |
| [5(ZnCl$_2\text{)}]  | CH$_3$CN   | 231, 283, 302, 424, 442        | 514                             | 3170                        |
|          | THF        | 231, 286, 304, 425, 445        | 498                             | 2390                        |

$^a$ Only the lowest-energy band is listed.

433 nm in Et$_2$O and 435 nm in THF) is blue-shifted with respect to 1, but still red-shifted with respect to unsubstituted phenazine (363 nm in CH$_3$CN). This fits with the expectations of a significantly higher HOMO energy in 1 compared with 5. The wavenumber of the emission maximum (568 nm in Et$_2$O, 599 nm in CH$_3$CN and 588 nm in THF) is much larger for 5. This leads to large Stokes shifts of 5490 cm$^{-1}$ in Et$_2$O, 8751 cm$^{-1}$ in CH$_3$CN and 5982 cm$^{-1}$ in THF. Compound 1 has an average fluorescence lifetime of 4.6(2) ns in CH$_3$CN, compared to 7.6(6) ns of compound 5 (see Table 2 and Fig. S4f). Interestingly, the average lifetimes are nearly independent of the excitation wavelength in CH$_3$CN.

Finally, we studied the absorption and emission spectra of compound 2. As example, Fig. 5 shows the spectra recorded for a CH$_3$CN solution. The lowest-energetic electronic transition occurred at 371 nm. The fluorescence signal was only weak (quantum yield below 0.01), with the maximum of emission at 428 nm and a long tail towards higher energies.

Quantum chemical calculations were carried out to analyse in more detail the influence of the guanidino groups on the shape and energies of the HOMO and LUMO orbitals of phenazine and fluorene. The isodensity surfaces for these orbitals are visualized in Fig. 4c and 5b. It can be seen that the guanidino groups contribute to the HOMO, especially in the case of 1. As expected, they cause a significant increase of the HOMO energies and a less strong increase of the LUMO energy. Consequently, the HOMO–LUMO gap shrinks from 3.66 eV in phenazine to 3.24 eV in 1 and from 4.99 eV in fluorene to 4.13 eV in 2. The decrease of the HOMO–LUMO gap is in line with the observed colour changes and the difference in the lowest-energetic transitions detected in the absorption spectra (484 nm for 1 and 371 nm for 2 in CH$_3$CN solution). It will be shown below that this band can indeed be assigned to the HOMO–LUMO excitation.

**Coordination chemistry**

Next we analysed the effect of metal coordination (especially d$^{10}$ metal ions) on the optical properties of the new phenazine derivatives. We started our work by comparing the luminescence of a solution of 1 upon addition of various metal salts, and observed quenching of the luminescence signal upon addition of Cu$^+$ salts, but a blue-shift of the signal in the presence of Ag$^+$ or Zn$^{11}$ salts. To find out more about the coordination of these metals, we carried out more directed experiments. The reaction between compound 1 and 2 eq. of CuI yielded the complex [I(Cu)$_2$] in a moderate yield of

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Table 1 Comparison of absorption and emission wavelengths (in nm) and Stokes shifts (in cm$^{-1}$) for 1, [I(ZnCl$_2\text{)}], 5 and [I(ZnCl$_2\text{)}] in different solvents

Table 2 Comparison of quantum yield $\Phi$, Stokes shifts (in cm$^{-1}$) and lifetime (in ns) for 1, [I(ZnCl$_2\text{)}], 5 and [I(ZnCl$_2\text{)}] in CH$_3$CN solutions

Fig. 5 (a) Electronic absorption and emission spectra for 2 in CH$_3$CN solution. (b) Calculated HOMO and LUMO energies (B3LYP/6-311G**) of 2 relative to unsubstituted fluorene.
ca. 50%. The lowest energy band in the absorption spectrum (see Fig. S5 of the ESI†) occurred at 493 nm in CH₃CN. This band has a shoulder at 465 nm, which we assign to excitation into an excited vibronic level (due to the difference of 1222 cm⁻¹ and the similar intensity ratios in all experiments). In CH₂Cl₂, the band maximum shifts only slightly to 501 nm.

An extremely weak luminescence signal (too weak to determine its quantum yield) was observed at 533 nm in CH₃CN and 519 nm in CH₂Cl₂. Hence the coordination of two CuI units caused a sharp decrease of the luminescence signal of compound 1 to almost vanishing point. This is surprising since CuI is a d¹⁰ metal ion (like ZnII and AgI), which normally does not lead to luminescence quenching. Often luminescence quenching by CuI is explained by disproportionation of CuI in solution into CuII and Cu. However, our results clearly show coordination of CuI. We strictly avoided air contact, so that oxidation of CuI to CuII could be excluded. In this case, we could not exclude the participation of a triplet state.

Reaction of 1 with two equivalents of ZnCl₂ gave a product which could be identified as the dinuclear complex [1(ZnCl₂)₂]. Fig. 6a displays its structure from single-crystal X-ray diffraction experiments. Again, the absorption spectrum of this complex showed little difference to that of free 1, with the lowest-energetic band measured at 484 nm in CH₃CN and 486 nm in CH₂Cl₂. However, in sharp contrast to the copper complex, the fluorescence signal remained strong. A quantum yield for fluorescence of 0.36 was measured in CH₃CN solution. The quantum yield of free 1 in CH₃CN solution amounts to only 0.22 (see Table 2). The increase of the quantum yield upon zinc coordination might point to the presence of a PET
mechanism in free 1, which is removed upon coordination (see the discussion in the Introduction). The emission maximum of [1(ZnCl₂)₂] was reached at 506 nm in CH₃CN and 512 nm in CH₂Cl₂, being significantly blue-shifted with respect to free 1 (568 nm). The Stokes shift decreases upon coordination in CH₃CN from 3060 cm⁻¹ (free 1) to 898 cm⁻¹. At the same time, the average fluorescence lifetime of [1(ZnCl₂)₂] in acetonitrile (1.8(4) ns) is drastically shorter than for 1 (4.6(2) ns) underlining the strong influence of coordination on the optical properties (see Table 2).

The corresponding mononuclear complex [5(ZnCl₂)] was also synthesized (see Fig. 6b). As for [1(ZnCl₂)₂], coordination leads to an increase of the imino C=N bond lengths (1.321(4)/1.312(4) Å in 5 and 1.345(3)/1.351(3) Å in [5(ZnCl₂)]). The metal atom is in plane with the phenazine core. Also in this case, the absorption spectrum is similar to that of the free ligand 5, and the lowest-energy band showed at 442 nm in CH₃CN and 445 nm (with a shoulder at 425 nm) in THF solutions. On the other hand, the emission spectrum clearly differs from that of the free ligand. Hence the maximum of emission is reached at 498 nm in THF and 514 nm in CH₃CN solutions (see Fig. 6c). The large Stokes shift observed for free 5 (8750 cm⁻¹ in CH₃CN) is greatly reduced upon zinc coordination (3169 cm⁻¹ for CH₃CN) (see also the data in Table 1). To highlight this difference, Fig. 6d compares the absorption and emission colours. The average fluorescence lifetime of [5(ZnCl₂)] in CH₃CN (1.3(5) ns) is also significantly reduced with respect to free 5 (7.6(6) ns).

When further ZnCl₂ was added to a solution of [1(ZnCl₂)₂] in CH₂Cl₂, the colour of the solution gradually changed from yellow to purple. In Fig. 7a, the UV/Vis spectra recorded for an experiment in which a concentrated solution of ZnCl₂ in CH₃CN was step-wise added to a CH₂Cl₂ solution of [1(ZnCl₂)₂] (c = 1.28 × 10⁻⁵ mol l⁻¹) is displayed, and the colour changes upon ZnCl₂ addition are shown underneath (Fig. 7b). The yellow-colored solution turned to intense purple upon addition of 2 eq. of ZnCl₂. In the UV/Vis spectra, the band at 486 nm with a shoulder at 459 nm decreased and gave way for an intense absorption at 581 nm and another one at 543 nm. The relative intensities of the two new absorptions varied and therefore

![Fig. 7](image-url)
they should belong to (at least) two different species in solution. In the case of solutions with low concentrations of \([1\text{ZnCl}_2]_2\) \((c = 0.64 \times 10^{-5} \text{ mol l}^{-1}\), see Fig. S6 in the ESI\(\text{f}\)), more equivalents of ZnCl\(_2\) were necessary to decrease the 486/459 nm band, pointing to an aggregation equilibrium. The obvious inference is that the excess ZnCl\(_2\) binds to the N atoms of the phenazine core and connects the \([1\text{ZnCl}_2]_2\) complex units to oligomeric chains or rings (see Scheme 5). Aggregation-induced changes in the optical properties of metal complexes were also observed in other cases.\(^{19}\) Indeed we were able to synthesize the complex \([1\text{ZnCl}_2]_3\) by reaction of 1 with 2.5 eq. of ZnCl\(_2\). Purple-colored crystals of this compound were grown from a CH\(_2\)Cl\(_2\)-Et\(_2\)O solvent mixture. Fig. 8 shows the molecular structure of \([1\text{ZnCl}_2]_3\) as derived from single-crystal X-ray diffraction. As expected, two \([1\text{ZnCl}_2]_3\) complex units are linked via a ZnCl\(_2\) unit. The Zn-N bond distances within the \([1\text{ZnCl}_2]_3\) units (in average 2.034 Å long) are shorter than the Zn-N bonds which link the \([1\text{ZnCl}_2]_1\) units together (2.099 Å in average). This result indicates that the latter bonds are weaker, in line with the observed equilibrium (see Scheme 5).

Quantum chemical calculations (B3LYP/def2-SV(P)) were carried out to obtain some preliminary information about the Gibbs free energy changes associated with the coordination of ZnCl\(_2\) to compound 1. For the first step, reaction of 1 with two equivalents ZnCl\(_2\) to give the dinuclear complex \([1\text{ZnCl}_2]_2\), a \(\Delta G\) value (at 298 K, 1 bar) of \(-365 \text{ kJ mol}^{-1}\) was calculated. For the second step, reaction of two \([1\text{ZnCl}_2]_2\) complex units with ZnCl\(_2\) to give the pentanuclear complex \([1\text{ZnCl}_2]_3\), we calculated a gas-phase Gibbs free energy change of \(-162 \text{ kJ mol}^{-1}\). The calculated \(\Delta G\) values neglect solvent effects, which are likely to be significant, especially in the case of ZnCl\(_2\). On the other hand, the difference in the Gibbs free energy changes between the first and the second step is in full agreement with the experimental results. According to Scheme 5, further aggregation might lead to a chain oligomer or polymer of the composition \([1\text{ZnCl}_2]_n\). Indeed, we observed the formation of a solid material for addition of a large excess of ZnCl\(_2\) (the precipitation started upon addition of four equivalents for a CH\(_2\)Cl\(_2\) solution of \([1\text{ZnCl}_2]_1\) with \(c = 1.28 \times 10^{-5} \text{ mol l}^{-1}\), and of ten equivalents for the lower concentration \((c = 0.64 \times 10^{-5} \text{ mol l}^{-1}\)). In preliminary experiments, we recorded a diffuse reflectance measurement of this solid embedded in a BaSO\(_4\) matrix. This spectrum (see Fig. S7 in the ESI\(\text{f}\)) displays electronic absorptions around 305, 455 and 545 nm (the latter as a shoulder and with a tail towards larger wavenumbers). The position of the 545 nm band fits quite well with the absorption at 543 nm measured in the solution spectra. In summary we explain the spectra shown in Fig. 7a as follows: the 486 nm band clearly belongs to \([1\text{ZnCl}_2]_1\), the 581 nm should belong to \([1\text{ZnCl}_2]_2\) and the 543 nm band is tentatively assigned to higher aggregates \([1\text{ZnCl}_2]_n\).

When the experiment was repeated with ZnBr\(_2\) in place for ZnCl\(_2\), we observed a similar reaction pattern. On the other hand, with ZnMe\(_2\) the reaction stopped at the stage of the dinuclear complex; aggregation was not observed. The Lewis acidity of ZnMe\(_2\) is obviously not high enough for additional coordination at the phenazine N atoms. We also carried out some quantum chemical calculations (again B3LYP/def2-SV(P)), which are fully consistent with the experimental results. Hence reaction between 1 and two eq. of ZnMe\(_2\) to give \[1\text{ZnMe}_2]_2\] is still mildly exergonic by \(-28 \text{ kJ mol}^{-1}\), but further reaction of two eq. of \([1\text{ZnMe}_2]_2\) with ZnMe\(_2\) is endergonic by \(+41 \text{ kJ mol}^{-1}\) (at 298 K, 1 bar). Hence only strong Lewis acidic metals are capable to form the aggregates.

In Fig. 9a, the absorption spectra of free 1, \([1\text{ZnCl}_2]_2\) and of a mixture of \([1\text{ZnCl}_2]_2\) together with 2 eq. of ZnCl\(_2\), all dissolved in CH\(_2\)Cl\(_2\), are compared. In Fig. 9b and 9c the TD-DFT spectra calculated with B3LYP/def2-SV(P) and BP/def2-SV(P),
respectively, for the three species 1, [1(ZnCl2)2] and [(1)_2(ZnCl2)_3] are shown. The calculations (see Tables S1 and S2 and Fig. S8–S10 in the ESI† for details) show that the lowest-energetic transition of 1 (observed at 487 nm in CH2Cl2 and calculated at 441 nm (B3LYP)/503 nm (BP)) and of [1(ZnCl2)2] (observed at 486 nm and calculated at 462 nm (B3LYP)/540 nm (BP)) can be assigned to more or less pure HOMO–LUMO excitations. The calculated spectra also predict correctly a red-shift of the lowest-energetic electronic transition upon formation of [(1)_2(ZnCl2)_3]. In the case of [(1)_2(ZnCl2)_3], a number of orbitals contribute to the lower energy electronic
transitions (see Table S1, Fig. S8 and S9 in the ESI†). The experimentally observed red-shift of 95 nm from \([\text{I}](\text{ZnCl}_2)_2\) to \([\text{I}](\text{ZnCl}_2)_3\) compared with a calculated one of ca. 40 nm (B3LYP)/48 nm (BP). In summary, the calculations fully support our assignment.

A number of additional measurements were made to obtain further information about the aggregation equilibrium. Due to the distinct color changes upon aggregation, we predominantly relied on UV/Vis spectroscopy as analytical technique. However, it should be noted that aggregation is also visible with other techniques. For example, in the aromatic region in the \(^1\text{H} \text{NMR} \) spectrum of \(\text{CD}_2\text{Cl}_2\) solutions, a signal at \(\delta\) (ppm) = 6.89 can be assigned to \([\text{I}](\text{ZnCl}_2)_2\), and two signals at \(\delta\) (ppm) = 7.04 and 6.71 to \([\text{I}](\text{ZnCl}_2)_3\). Higher aggregates are responsible for signals at \(\delta\) (ppm) = 8.65 and 6.11. 2D HSQC experiments (HSQC = Heteronuclear Single Quantum Coherence) proved all these signals to arise from C–H protons, but a more detailed assignment was not possible.

The complex \([\text{I}](\text{ZnCl}_2)_3\) was dissolved in different solvents. The colour of the solution varied between yellow (in THF) and pink (in CHCl\(_3\)) (see Fig. 10b). The reason for the different colors can be found in differences in the degree of aggregation. Hence THF could compete successfully with \([\text{I}](\text{ZnCl}_2)_2\) in coordinating to \(\text{ZnCl}_2\), and consequently the solution mainly consists of \([\text{I}](\text{ZnCl}_2)_3\). We observed that an initially pink-colored solution in THF in minutes changed colour to yellow, showing that THF not only prohibits aggregation, but also could break up the aggregates. On the other hand, CHCl\(_3\) solutions mainly consist of aggregates; the band due to \([\text{I}](\text{ZnCl}_2)_3\) at 486/459 nm is relatively small. Additional experiments were carried out in which the concentrations were varied for all three solvents (see Fig. S11 in the ESI†). These experiments show that the percentage of aggregates increases with increasing concentration (as already discussed for \(\text{CH}_2\text{Cl}_2\)), in line with the presence of an equilibrium. The effect of temperature on the relative band intensities turned out to be much weaker, and only slight variations were observed in the temperature region \(-60-\{+20\}\) °C in \(\text{CH}_2\text{Cl}_2\) solution.

Finally, we inspected the fluorescence properties of aggregate mixtures. Fig. 11 displays the fluorescence signals measured for a solution of \([\text{I}](\text{ZnCl}_2)_3\) in \(\text{CH}_2\text{Cl}_2\). Two fluorescence signals were detected, one at 506 nm, which belongs to the dinuclear complex \([\text{I}](\text{ZnCl}_2)_2\), and another one at 599 nm. Measurements with different excitation wavelengths (see Fig. 11) clearly showed that the 581 nm absorption is the corresponding band of this species in the UV/Vis spectrum, and therefore the fluorescence signal at 599 nm could be assigned to the complex \([\text{I}](\text{ZnCl}_2)_3\) (Stokes shift of 517 cm\(^{-1}\)). We could qualitatively state that coordination at the phenazine N atoms greatly reduces the fluorescence quantum yield, although the absolute quantum yield for \([\text{I}](\text{ZnCl}_2)_2\) cannot be determined due to the equilibrium. The oligomeric or polymeric \([\text{I}](\text{ZnCl}_2)_3\) is fluorescence silent, and therefore the 543 nm band in the absorption spectra has no equivalent in the emission spectra. Our results show that the electronic and optical properties of the new fluorescent dye 1 could be greatly influenced by coordination.

Conclusions

Guanidino groups could be effectively used to tune the optical properties of aromatic compounds. They are a valuable alternative to the traditionally employed amino groups, which they outperform in several aspects. The guanidino groups decrease the HOMO–LUMO gap, increase the fluorescence quantum yield, and offer sites for metal coordination. In this work we show that substitution of phenazines with guanidino groups leads to highly fluorescent dyes. The absorption and emission spectra were studied in detail in several solvents. The Stokes shifts vary with the solvent and shifts of 2130–8750 cm\(^{-1}\) were measured. Especially remarkable are the Stokes shifts of 5040 cm\(^{-1}\) for 1 in H\(_2\)O and of 8750 cm\(^{-1}\) for 5 in CH\(_3\)CN. The quantum yield for fluorescence reaches a record value of 0.39 for 1 dissolved in Et\(_2\)O. In contrast to the highly-fluorescent guanidino-functionalized phenazines, the guanidino-substituted fluorene 2, which was also synthesized in this work,
shows little fluorescence. The bisguanidino-phenazine 5 also is a strongly fluorescent dye, but the fluorescence quantum yield is lower than for 1. We note that the extremely large Stokes shifts measured for 5 (up to 8750 cm\(^{-1}\)) together with the relatively low wavenumber of the lowest-energetic transition in the UV/Vis spectrum might qualify the compound for applications in electroluminescent devices (see the discussion in ref. 34).

The influence of coordination at the guanidino groups of the phenazine systems on the optical properties was subsequently analyzed. Cu\(^{2+}\) coordination leads to luminescence quenching. By contrast, coordination with ZnCl\(_2\) leads to intensely fluorescent metal complexes. Both the dinuclear complex [1(ZnCl\(_2\))]\(_2\) and the mononuclear complex [5(ZnCl\(_2\))] were structurally characterized. While little changes were observed in the absorption spectra upon coordination, the Stokes shifts decrease significantly. Also, the fluorescence lifetimes of 1 and 5 in CH\(_3\)CN are dramatically reduced by coordination of ZnCl\(_2\). The measured lifetimes are independent of the excitation wavelength which makes these compounds highly interesting for further spectroscopic studies. For the strong Lewis basic compound 1, an excess of ZnCl\(_2\) initiates aggregation in the course of which the dinuclear [1(ZnCl\(_2\))]\(_2\) complex units are connected by ZnCl\(_2\). The degree of aggregation is strongly solvent dependent. Aggregation is accompanied by a color change from yellow to purple, and the UV/Vis spectra displays lower-energetic bands. We were able to structurally characterize the compound [(1)\(_2\)(ZnCl\(_2\))]\(_5\), in which two [1(ZnCl\(_2\))] units are connected via a ZnCl\(_2\) bridge. In ongoing work we are extending our studies to other guanidino-substituted fluorescent dyes.

Experimental details

If not stated otherwise, the reactions were carried out under Ar atmosphere using Schlenk techniques. Solvents were dried prior to use by standard methods, and preserved over 4 Å molecular sieves. NMR spectra were measured with Bruker Avance II 400 or Bruker Avance DPX AC200 NMR machine. Elemental analyses were carried out at the Microanalytical Laboratory of the University of Heidelberg. IR spectra were recorded with a Biorad Excalibur FTS 3000 spectrometer. UV/Vis measurements were recorded with a Varian Cary 5000 UV/Vis/NIR spectrophotometer. Fluorescence measurements were recorded with a Varian Cary Eclipse machine. Fluorescence quantum yields were obtained by using fluoresceine in 0.1 M NaOH as standard (\(\Phi = 0.82\)).\(^{36}\) Fluorescence lifetimes were determined with a PicoQuant FluoTime 100 Compact Fluorescence Lifetime spectrometer. Fluorescence excitation was performed with a 280 nm pulsed LED at 10 MHz repetition rate. Electrochemical studies were carried out at r.t. using an EG&G model 273A potentiostat/galvanostat. The auxiliary electrode was a platinum wire and the working electrode was a glassy carbon disk. The reference electrode was an aqueous Ag/AgCl in 3 M KCl electrode. A Bruker ApexQe FT-ICR (ESI) machine was used for mass spectrometry.

2,3,7,8-Tetrakis(tetramethylguanidino)phenazine, 1 (in three steps)

1. **Step** (2,3,6,7-tetraamino-phenazine): this compound was prepared as described in the literature.\(^{25}\) Briefly, 1,2,4,5-tetraamino-benzene-tetrahydrochloride (1.338 g, 4.712 mmol) were dissolved in 30 mL distilled water. Then 3.091 g sodium acetate (37.69 mmol) were added. The reaction mixture was heated to reflux, while passing compressed air though the solution. After 5h, the reaction mixture was cooled to room-temperature, during which time a deep purple colored solid precipitated. The solid was separated by filtration, washed with water and dried under vacuum. Yield: 0.733 g (2.097 mmol, 89%). Elemental analysis for 2·(2,3,6,7-tetraamino-phenazine)·3HCl, C\(_23\)H\(_{26}\)Cl\(_2\)N\(_{12}\) (349.65): calcd C 48.86, H 4.61, N 28.49; found C 48.27, H 4.63, N 27.71. 1H NMR
(200 MHz, d4-DMSO): δ (ppm) = 5.47 (s, 8 H, NH2), 6.78 (s, 4 H, Har). MS (EI†): m/z = 241.4 u [M + H]+, 100%.

2. Step (2-chloro-1,1,3,3-tetramethylformamidinium chloride, [CIC(NMe2)2]Cl): oxalylchloride (0.965 ml, 11.25 mmol, 0.228 g) was added drop-wise to a solution of 0.270 ml CH2Cl2. The pale yellow reaction mixture was heated to reflux for a period of 16h, and then allowed to cool to room temperature. Subsequently the solvent was removed under vacuum and the solid residue washed three times with 19 mL portions of EtO. Finally the activated urea was used directly after filtration and subsequently for the guanidinylation reaction.

3. Step (2,3,7,8-tetrakis(tetramethylguanidino)phenazine, 1): 0.745 ml (5.400 mmol) NEt3 was added to a solution of 0.133 g (0.45 mmol) 2,3,7,8-tetramino-phenazine-1.5HCl in 0.05 mL CH3CN. To this suspension a solution of 0.385 g (2.250 mmol) 2-chloro-1,1,3,3-tetramethylformamidinium chloride in 10 mL CH2Cl2 was added. The reaction mixture was stirred for a period of 5 h at a temperature of 60 °C, leading to the precipitation of a brown-colored solid. After removal of the solvent under vacuum, the pale-brown solid was dissolved in destilled water. Upon addition of 25% NaOH solution, an orange-brown solid precipitated, which was extracted with CHCl3. The CHCl3 solution was dried over K2CO3 before the solvent was removed under vacuum. Yield of crude product: 0.199–0.227 g (0.314–0.359 mmol, 70–80%). Recrystallization from toluene at –18 °C afforded the orange-colored solid product in a yield of up to 74%. Deep-orange colored crystals were obtained from Et2O solutions at room temperature. Solutions of the yellow-orange colored. Elemental analysis for C25H30N4 (436.85) calculated C 72.97, H 6.92, N 14.76%. MS (ESI+): m/z = 435.3 u ([M + Na]+, 67%), 417.2 u ([M + K]+, 67%). The 2,7-diamino-fluorene·2HCl was separated from the solution by filtration and subsequently washed three times with 10 mL portions of concentrated HCl solution. 1H NMR (200 MHz, d4-DMSO): δ (ppm) = 7.92 (d, 2 H, J = 8.2 Hz, H8ar), 7.47 (s, 2 H, H6ar), 7.28 (d, 2 H, J = 8.2 Hz, H8ar), 4.00 (s, 2 H, CH2). 13C NMR (150 MHz, d4-DMSO): δ (ppm) = 121.95 (C6ar), 121.08 (C4ar), 120.02 (C3ar), 36.36 (CH2). MS (FAB): m/z = 196.5 u [M]+, 100%. MS (ESI+): m/z = 197.2 u [M + H]+, 100%. The 2,7-diamino-fluorene·2HCl was dissolved in H2O and a saturated NaHCO3 solution was added until a pH value of 8 was reached. The yellow precipitate of 2,7-diamino-fluorene was separated by filtration, dried under vacuum and used in the next step without further purification.

1H NMR (200 MHz, d4-DMSO): δ (ppm) = 7.25 (d, 2 H, J = 8.0 Hz, H8ar), 6.68 (s, 2 H, H6ar), 6.49 (d, 2 H, J = 8.0 Hz, H8ar), 4.87 (br s, 4 H, NH2), 3.57 ppm (s, 2 H, CH3).

2. Step (2,7-diacetamido-fluorene): 1.532 g (7.806 mmol) of 2,7-diacetamido-fluorene were suspended in 25 mL CH2Cl2. The pale yellow reaction mixture was heated to reflux for an additional 10 min the solution was poured on ice. The color of the mixture changed from white to deep-green. After complete addition of the HNO3·CH2Cl2 solution it slowly bleached and an orange-colored precipitate formed. After stirring for an additional 10 min the solution was poured on ice. The yellow-colored precipitate was separated by filtration and washed with some H2O, yielding 67% of 3,6-dinitro-2,7-diacetamido-fluorene (2,7-diamino-fluorene·2HCl).

3. Step (3,6-dinitro-2,7-diacetamido-fluorene): 1.703 g (6.073 mmol) 2,7-diacetamido-fluorene were suspended in 40 mL CH2Cl2. After addition of 35 mL glacial acetic acid the mixture was cooled to −10 °C, and a −10 °C cold solution of 17.5 mL fuming nitric acid in 50 mL CH2Cl2 drop-wise slowly added, keeping the temperature below −5 °C. The color of the mixture changes first from white to deep-green. After complete addition of the HNO3·CH2Cl2 solution it slowly bleached and an orange-colored precipitate formed. After stirring for an additional 10 min the solution was poured on ice. The yellow-colored precipitate was separated by filtration and washed with some H2O, yielding 67% of 3,6-dinitro-2,7-diacetamido-fluorene. 1H NMR (200 MHz, d4-DMSO): δ (ppm) = 10.30 (s, 2 H, NH), 8.73 (s, 2 H, H8ar), 7.89 (s, 2 H, H8ar), 4.21 (s, 2 H, CH2), 2.11 (s, 6 H, CH3). MS (EI+): m/z = 129 (M+, 100%); 103 (M - CH2O, 79%); 91 (M - CO2, 45%).
7 h to a temperature of 75 °C, leading to a color change from orange to deep-red. The reaction mixture was allowed to cool back to room temperature and then poured on ice. The deep-red colored precipitate was separated by filtration and dried under vacuum, yielding 78% of 3,6-dinitro-2,7-diaminofluorene. $^1$H NMR (200 MHz, d$_6$-DMSO): δ (ppm) = 8.41 (s, 2 H, H$_{ar}$), 7.54 (br s, 4 H, NH$_2$), 7.09 (s, 2 H, H$_{ar}$), 3.96s, 2 H, CH$_2$).

4. Step (2,3,6,7-tetramino-fluorene-4HCl): 4.5 mL concentrated HCl solution was added to a suspension of 0.148 g (0.516 mmol) of 3,6-dinitro-2,7-diaminofluorene-4HCl in 5 mL EtOH. The pale-yellow colored precipitate of 2,3,6,7-tetramino-fluorene·4HCl was separated by filtration and dried back to room temperature and then poured on ice. The deep-brown solid was dissolved in 10% HCl solution. Upon the addition of 25% NaOH solution, the deep-brown solid was re-dissolved in water. The product was then precipitated by addition of 25% NaOH solution, and subsequently extracted 5 times with 15 mL portions of CHCl$_3$. The organic phase was dried over K$_2$CO$_3$, and then the solvent was removed under vacuum to obtain 2,3,6,7-tetramino-fluorene·4HCl in a yield of 58%. $^1$H NMR (200 MHz, d$_4$-CD$_3$CN): δ (ppm) = 7.90 (s, 2 H, H$_{ar}$), 7.62 (s, 2 H, H$_{ar}$), 4.08 (s, 2 H, CH$_2$). MS (HR-ESI): m/z = 226.12128 ([M]$^+$, 100%).

5. Step (2,3,6,7-Tetrakis(N,N$^\prime$,N$^\prime$$\prime$,N$^\prime$$\prime$$\prime$-tetramethylguanidinio)-fluorene, 2): 0.546 g (5.400 mmol) NEt$_3$ were added to a solution of 0.102 g (0.450 mmol) 2,3,6,7-tetramido-fluorene-tetraydrochloride in 5 mL CH$_3$CN. This suspension was cooled at 0 °C. To this suspension, a solution of 2.250 mmol of 2-chloro-1,1,3,3-tetramethylguanidinium chloride in 8 mL CH$_3$CN was added. The reaction mixture was stirred for a period of 2 h at a temperature of 0 °C, leading to the precipitation of a brown-colored solid. After removal of the solvent under vacuum, the light-brown solid was dissolved in 10% HCl solution. Upon the addition of 25% NaOH solution, the aqueous solution was extracted with Et$_2$O (4 × 15 mL), and the organic phases were dried over K$_2$CO$_3$. The solvent was removed under vacuum, and the crude product as yellow-brown solid was dried under vacuum. The purification was carried out by sublimation at 210–220 °C and the white solid was obtained. Yield: 0.162 g (0.261 mmol, 58%). Elemental analysis for C$_{33}$H$_{54}$N$_{12}$: calcd C 64.05, H 8.79, N 27.16; found C 64.05, H 8.76, N 27.16. UV/Vis (CH$_3$CN, 15 mL portions of CHCl$_3$): $\lambda_{max}$ (CM), 310.23 (100%), $\phi$ = 3.84. IR (CsI): $\tilde{\nu}$ = 3432, 2953, 1691, 1582, 1437, 1202, 1071, 910, 752 (cm$^{-1}$). Fluorescence (CH$_3$CN): $\lambda_{em}$ = 395 nm; Fluorescence (THF, $\lambda_{ex}$ = 444 nm): $\lambda_{em}$ = 588 nm. Quantum yield: $\Phi$ (THF) = 0.17, $\Phi$ (CH$_3$CN) = 0.15, $\Phi$ (Et$_2$O) = 0.11. Crystal data for $\text{C}_{22}$H$_{31}$N$_{8}$: Mr = 407.26683, di $\phi$ = 1.136 Mg m$^{-3}$, monoclinic, space group $P2_1/c$, $a$ = 15.900(3), $b$ = 9.2100(18), $c$ = 16.379(3) Å, $\beta$ = 94.82(3)$^\circ$, $V$ = 2390.0(9) Å$^3$, $Z$ = 4, $d_{calc}$ = 1.230 Mg m$^{-3}$, Mo Kα radiation (graphite monochromated, $\lambda$ = 0.71073 Å), $T$ = 100 K, $\theta_{range}$ 2.21 to 30.04°. Reflections measured. 31 289, indep. 8875, $R_{int}$ = 0.0820. Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0673$, $wR_2 = 0.1721$.
addition of Et2O precipitated as a clean product. The product was filtrated and dried under vacuum. Yield: 0.055 g (0.0359 mmol, 51%). Elemental analysis for C_{32}H_{52}Cl_{4}N_{14}Zn_{2} (1013.75): calc C 37.91, H 5.17, N 19.34; found C 37.65, H 5.06, N 19.18. MS (HR-ESI^+): m/z = 823.29278 u ([C1 + Cu + H]^+), 20.5%, 950.12976 u ([C1 + Cu + 2H]^+), 14.7%. MS (FAB^+): m/z = 588.6 ([N - Me]2^+), 21.2%, 633.5 u ([H + H]^+), 9.6%, 696.1 u ([C + Cu]^+), 17.3%, 824.0 u ([C + Cu + 2H]^+), 13.5%, 1012.7 u ([M]^+), 9.6%. UV/Vis (CH2Cl2, c = 0.9081 × 10^{-5} mol l^{-1}, d = 1 cm): \lambda_{max} (\epsilon, in L mol^{-1} cm^{-1}) = 226 (6.067 × 10^{4}), 243 (5.7190 × 10^{4}), 317 (7.4615 × 10^{4}), ca. 465 (3.4082 × 10^{4}, shoulder), 493 nm (5.9110 × 10^{4}) nm. UV/Vis (CH3CN, c = 1.3042 × 10^{-3} mol l^{-1}, d = 1 cm): \lambda_{max} (\epsilon, in L mol^{-1} cm^{-1}) = 321 (8.8200 × 10^{6}), ca. 474 (4.2945 × 10^{6}, shoulder), 501 (7.7254 × 10^{6}) nm. Fluorescence signals almost extinguished by CuI coordination. Fluorescence (CH3Cl2, \lambda_{ex} = 460 nm): \lambda_{max} = ca. 519 nm. Fluorescence (CH3CN, \lambda_{ex} = 465 nm): \lambda_{max} = ca. 533 nm. IR (CsI): \nu (\text{cm}^{-1}) = 166.23 (C\text{C\text{C}}), 1411 (C\text{ar\text{H}}), 1326 (C\text{ar\text{H}}), 1199m, 1157m, 1142m, 1108w, 1064w, 1026m, 958w, 917w, 905w, 855w, 796w, 785w, 740w, 733w, 714w, 696w, 668w, 610m, 502w cm^{-1}. 

\[[\text{ZnCl}_{2}]\]_{0} 0.0256 g (2 eq., 0.1878 mmol) of ZnCl2 was dissolved in 2 mL CH2CN and added dropwise to a solution of 0.0594 g (0.0939 mmol) of 1 in 2 mL CH2CN. The reaction mixture was stirred for a period of 2 h at room temperature. The solvent was removed to obtain an orange solid that was redissolved in 1.5 mL CH2Cl2 and filtered to remove the insoluble rest. Upon addition of Et2O the product precipitates as a crystalline orange solid. The product was filtered, washed three times with 1 mL portions of Et2O and dried under vacuum. Upon recrystallization from CH2Cl2 crystals of [1(ZnCl2)] were obtained. Yield 0.0450 mg (0.0498 mmol, 53%) product. Elemental analysis for C_{32}H_{52}Cl_{4}N_{14}Zn_{2} (905.42): calcd C 38.70, H 5.79, N 19.21; found C 38.66, H 5.66, N 21.26.

1H NMR (600 MHz, CD2Cl2): \delta (ppm) = 6.89 (8, 4 H, H_{ar}), 3.03 (8, 24 H, Me), 2.84 (8, 24 H, Me). 13C NMR (150 MHz, CD2Cl2): \delta (ppm) = 166.23 (C\text{guan}), 145.94 (C\text{ar\text{H}}), 141.51 (C\text{ar\text{H}}), 113.02 (C\text{ar\text{H}}), 41.21 (C\text{ar\text{H}}), 40.52 (C\text{ar\text{H}}). 1H NMR (600 MHz, CD2Cl2): \delta (ppm) = 6.88 (8, 4 H, H_{ar}), 3.06 (8, 24 H, Me), 2.90 (8, 24 H, Me). 13C NMR (150 MHz, CD2Cl2): \delta (ppm) = 165.74 (C\text{guan}), 144.61 (C\text{ar\text{H}}), 141.09 (C\text{ar\text{H}}), 112.55 (C\text{ar\text{H}}), 41.17 (C\text{ar\text{H}}), 40.38 (C\text{ar\text{H}}). UV/Vis (CH2CN, c = 1.1486 × 10^{-5} mol l^{-1}, d = 1 cm): \lambda_{max} (\epsilon, in L mol^{-1} cm^{-1}) = 226 (6.8925 × 10^{4}), 316 (7.6583 × 10^{4}), 458 (3.7518 × 10^{4}), 484 (5.7725 × 10^{4}) nm. UV/Vis (CH3CN, c = 1.4137 × 10^{-7} mol l^{-1}, d = 0.5 cm): \lambda_{max} (\epsilon, in L mol^{-1} cm^{-1}) = 228 (5.3921 × 10^{4}), 319 (6.9684 × 10^{4}), 459 (3.5629 × 10^{4}), 486 (5.4647 × 10^{4}) nm. Fluorescence (CH2CN, \lambda_{ex} = 484 nm): \lambda_{max} = 506 nm. Fluorescence (CH3Cl2, \lambda_{ex} = 486 nm): \lambda_{max} = 512 nm. Quantum yield: \Phi(CH2CN) = 0.36. IR (CsI): \nu (\text{cm}^{-1}) = 1323 (\text{C\text{C\text{C}}}), 1234 (\text{C\text{ar\text{H}}}), 1157 (\text{C\text{ar\text{H}}}), 1043 (\text{C\text{ar\text{H}}}), 1012 (\text{C\text{ar\text{H}}}), 960 (\text{C\text{ar\text{H}}}), 897 (\text{C\text{ar\text{H}}}), 815 (\text{C\text{ar\text{H}}}).
V = 5455.9(19) Å³, Z = 2, d_{calc} = 1.428 Mg m⁻³, Mo Kα radiation (graphite monochromated, λ = 0.7073 Å), T = 100 K, θ_{range} 2.48 to 27.52°. Reflections measured. 45 548, independent. R_{int} = 0.0342. Final R indices [I > 2σ(I)]: R1 = 0.0633, wR2 = 0.1829.

X-ray crystallographic study

Suitable crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil and fixed on top of a cryo loop. Measurements were made with a Nonius-Kappa CCD diffractometer with low-temperature unit using graphite-monochromated Mo Kα radiation. The temperature was set to 100 K. The data collected were processed using the standard Nonius software. All calculations were performed using the SHELXT-PLUS software package. Structures were solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program. Graphical handling of the structural data during solution and refinement was performed with XPMA. Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares calculations. CCDC-1016464 (1), 1016465 (2), 1034621 ([1][ZnCl₂]), 1016466 ([5][ZnCl₂]), 1016467 (5·H₂O), 1016468 ([H₂][BF₄]₂), and 1016832 ([1][ZnCl₂]), contain the supplementary crystallographic data for this paper.

Details of the quantum chemical calculations

The density functional calculations on the uncoordinated compounds and protonated 1 were carried out with the B3LYP functional⁴¹ and the 6-311G* basis set. The GAUSSIAN⁴³ program package was used. To speed up the investigation for the different complexes, the calculations, including the TD-DFT calculations, were performed with the smaller def2-SV(P) basis set⁴⁴ in combination with the BP86⁴⁰,⁴⁵ and B3LYP functionals. The structures were optimized with the BP86 functional, using the resolution of the identity (RI) approximation and the appropriate auxiliary SV(P) basis set.⁴⁶ Then final energies were obtained with the B3LYP functional using thermodynamic contributions from the BP86 results. These calculations used the TURBOMOLE⁴⁷ program package.

A comparison of the structures (Table S2 in the ESI) and the HOMO–LUMO gap of compound 1 shows that in the case of the structure the usage of a different basis set and functional and in the case of the HOMO–LUMO gap the usage of a different basis set has only a minor impact on the calculated quantities. Within the B3LYP/6-311G** calculations the HOMO–LUMO gap amounts to 3.24 eV, whereas within the B3LYP/def2-SV(P) calculations it amounts to 3.16 eV.

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