Towards a New Family of Photoluminescent Organozinc 8-Hydroxyquinolinates with a High Propensity to Form Noncovalent Porous Materials

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Abstract: We report on investigations of reactions of tBu_2Zn with 8-hydroxyquinoline (q-H) and the influence of water on the composition and structure of the final product. A new synthetic approach to photoluminescent zinc complexes with quinolinate ligands was developed that allowed the isolation of a series of structurally diverse and novel alkylzinc 8-hydroxyquinolate complexes: the trinuclear alkylzinc aggregate [tBuZn(q)]₃ (1₃), the pentanuclear oxo cluster [(tBu)₃ $Zn_5(\mu_4$ -O)(q)₅] (2), and the tetranuclear hydroxo cluster [$Zn(q)_2$]₂[tBuZn(OH)]₂ (3). All compounds were characterized in solution by ¹H NMR, IR, UV/Vis, and photoluminescence (PL) spectroscopy, and in the solid state by X-ray diffraction, TGA, and PL studies. Density functional theory calculations were also carried out for these new Zn^{II} complexes to rationalize their luminescence behavior. A detailed analysis of the supramolecular structures of **2** and **3**

Keywords: density functional calculations • fluorescence • hydroxyquinoline • porous materials • zinc

Introduction

Advances in chemistry and physics are providing an expanding array of photoluminescent materials with unique and powerful optical properties. Ligand-based fluorescent coordination compounds have attracted a vast amount of attention due to their applications especially in modern electronics as material to produce organic light-emitting diodes

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shows that the unique shape of the corresponding single molecules leads to the formation of extended 3D networks with 1D open channels. Varying the stoichiometry, shape, and supramolecular structure of the resulting complexes leads to changes in their spectroscopic properties. The closepacked crystal structure of $\mathbf{1}_3$ shows a redshifted emission maximum in comparison to the porous crystal structure of $\mathbf{2}$ and the THF-solvated structure of $\mathbf{3}$.

(OLEDs).^[1] In particular, tris(8-hydroxyquinolinato)aluminum (Alq₃) is one of the most famous and widely used as the emitting and electron-transporting material among OLEDs.^[1a-d] With regard to the study described herein, it is also pertinent to note that more recently, bis(8-hydroxyquinolinato)zinc (Znq_2) ^[2] as well as a number of $Zn(L_2)$ homoleptic complexes based on 8-hydroxyquinoline derivatives^[2a,3] or other photoactive ligands have also been investigated as electroluminescent materials.^[4] Generally, the fluorescence properties of metal derivatives of 8-hydroxyquionoline (q-H) in the solid state are dependent, in particular, on the character of the metal ion, degree of aggregation, molecular and crystal structure, as well as the intermolecular noncovalent interactions involved.^[1a,c,5] Nevertheless, homoleptic Mq_n-type complexes provide relatively limited possibilities for tuning their photophysical properties that are essentially determined by their molecular structure and bulk molecular packing characteristics. Therefore, the development of new synthetic methods that lead to well-defined heteroleptic molecular complexes or polynuclear clusters supported by quinoline ligands, with novel core structures and unique self-assembly properties, and following improved and controllable photoluminescence features is a big challenge for chemists. In this regard organometallic complexes with reactive M-C bond are attractive candidates for this task due to the fact that they themselves may show fluores-

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cence properties and can also be potentially used as convenient precursors for further structural modifications by M-C bond functionalization into novel species with desired properties. However, the chemistry of organometallic complexes with bidentate quinolinate ligands, including related zinc compounds, remains surprisingly poorly explored,^[6] which significantly hampers the possibility of obtaining novel fluorescent polynuclear metal complexes supported by quinoline ligands by transformations of organometallic entities.

In the course of our systematic investigation on the structure and reactivity of organozinc complexes,^[7] we report, herein, on reactions of tBu₂Zn with q-H and the influence of water on the final composition and structure of the resulting products. In addition, we describe characterization of their absorption and emission properties in solution and the solid state along with the corresponding density functional theory (DFT) calculations.

Results and Discussion

Synthesis: During our preliminary investigations of the reaction between tBu₂Zn and a commercial grade 8-hydroxyquinoline (q-H), that is, crude, as received (Aldrich), we repeatedly observed the formation of a mixture of the expected tert-butylzinc complex stabilized by the quinolinate ligand, $[tBuZn(q)]_3$ (1₃) and surprisingly an organozinc oxo cluster, $[(tBu)_3Zn_5(\mu_4-O)(q)_5]$ (2; Scheme 1). The resulting compounds $\mathbf{1}_3$ and $\mathbf{2}$ were easily separated by fractional crystallization. Compound 2 precipitated in a moderate yield from the reaction mixture upon cooling to 4°C and it was a repro-

> tBu (он ċн path I q-H purified tBu₂Zn 1. q-H path II 2. H₂O q-H * H_oO path III commercia tBu 1, tBu path IV 2 3

Scheme 1. The synthesis pathways of zinc 8-hydroxyquinoline derivatives 1_3 , 2, and 3.

oxygen source responsible for the formation of 2 in the pres-

(Scheme 1, path II).

ent case. We anticipated that it was more likely to be a reaction with water contaminant in the commercial organic proligand that led to the formation of the oxo cluster. Supporting evidence for such a reaction scheme was obtained from further experiments involving purification of 8-hydroxyquinoline. Both a simple crystallization from toluene solution as well as sublimation of the commercial q-H were ineffective showing that the purification of this reagent is a demanding task. Similarly, dissolution of the proligand in toluene and stirring with a sodium-potassium alloy for several hours at ambient temperature or even severe vacuum conditions for three days under P2O5 did not remove the contaminating water. Finally, a solution of 8-hydroxyquinoline in toluene was refluxed with P_2O_5 for 2 h and this gave a positive result. The addition of q-H purified by the latter method to a solution of tBu₂Zn in toluene resulted in essentially quantitative formation of 1_3 without any traces of 2 (Scheme 1, path I). Note that for all of the mentioned reaction systems a standard Schlenk technique was used with the same batches of solvent. Thus, this is an additional strong indication that the contaminating water was acting as an oxide source in the formation of **2**.

ducible result throughout different batches of crude q-H

Given our previous studies concerning the oxygenation of

alkylzinc compounds,^[7a-g] it was reasonable for us to consid-

er that traces of molecular oxygen are less likely to be the

Organozinc compounds are usually highly reactive toward water, however systematic investigations of their hydrolysis are essentially lacking. As a consequence, there is a very

> limited number of well-characterized zinc complexes with an incorporated hydroxide group derived from the intentional or accidental hydrolysis of organozinc complexes.^[7h,8] The latter fact as well as the above-mentioned preliminary observations prompted us to carry out a thorough examination of water interactions with the tBu₂Zn/q-H reaction system. The reaction of freshly dissolved 1_3 in toluene with H₂O in a 2:3 molar ratio was carried out in a twophase reaction system with vigorous stirring and reproducibly afforded the unprecedented alkylzinc hydroxide supported by the quinolinate ligands, $[Zn(q)_2]_2[tBuZn(OH)]_2$ (3)(Scheme 1, path III). Notably, complex 3 was also isolated in high yield when an excess of water was used, which indicates the relative stability of 3 toward

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further hydrolysis. In the next control experiment, we mixed toluene solutions of 1_3 and 3 in a molar ratio 2:1 affording 2 almost quantitatively (Scheme 1, path IV). Thus, the experiment confirms that a ZnOH unit can be readily involved into the formation of an oxo species in the presence of a *t*BuZn unit.

Structure characterization: Compounds 1_3 , 2, and 3 were characterized in solution by ¹H NMR and IR spectroscopy (see the Experimental Section). The presence of a hydroxyl group in 3 is substantiated in the ¹H NMR spectrum (in [D8]THF) by a singlet resonance at $\delta = 3.20$ ppm and in the IR spectrum (CH₂Cl₂ solution) by a sharp O-H stretching band at 3530 cm^{-1.[7h]} In addition we carried out molecular weight measurements for $\mathbf{1}_3$ freshly dissolved in benzene.^[9] Cryoscopic molecular weight determinations revealed that, indeed, compound 1 occurs essentially in a trimeric form 1_3 with small amounts of lower aggregates in benzene solution (the calculated value for the trimer is 799.6 amu, whereas the value found experimentally is 746 ± 8 amu (n = 2.8); for theoretical calculations of the relative energies for various aggregates of 1 see below). This observation is consistent with the early study of Boersma and Noltes, which indicated that ethylzinc and phenylzinc derivatives of 8-hydroxyquinoline occur as trimeric species in benzene solution.^[10] Thus, it appears that the character of the alkyl group bonded to zinc in alkylzinc derivatives of 8-hydroxyquinoline has little effect on their structure in solution.

The X-ray diffraction studies of 1_3 , 2, and 3 were carried out to determine the degree of aggregation, the presence or absence of intermolecular noncovalent interactions, and other pertinent structural details. The molecular structure of $\mathbf{1}_3$ is shown in Figure 1 a, and the selected bonds lengths and angles are given in Table S1 in the Supporting Information. Compound $\mathbf{1}_3$ crystallizes in the $P2_1/c$ space group and its molecular structure consists of three discrete monomeric units bridged by the oxygen atoms of the chelating quinoline ligands. The central core comprises a puckered six-membered Zn₃O₃ ring with the coordination environment of ZnCNO₂ zinc atoms distorted from an ideal tetrahedral geometry due to the small bite angle of the quinoline ligand. The fourth coordination site on each zinc center is filled by the pyridine nitrogen atom of the quinolinate ligand. The Zn-N and Zn-O distances (average 2.105 and 2.036 Å, respectively) are similar to that observed in the tetrameric $Zn(q)_2$.^[11] The supramolecular structure of **1**₃ is presented in Figure 1b. It consists of noncovalently bonded dimers in which the association of the molecular moieties is attained through π -stacking (3.513 Å) interactions between the quinolinate rings (dotted lines in Figure 2).

The molecular structure of **2** is shown in Figure 2 a, and the selected bond lengths and angles are given in Table S2 (SI). Compound **2** crystallizes in the *P*-1 space group and exists as an pentanuclear cluster centered by the encapsulated μ_4 -O²⁻ ion. Formally its composition may be viewed as a cluster in which ZnO molecule is entrapped by three parent *t*BuZn(q) moieties and one bischelate Zn(q)₂ moiety.



Figure 1. a) Molecular structure of $\mathbf{1}_3$; hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: O1–Zn1, 2.081(2); O1–Zn2, 1.996(2); O2–Zn2, 2.071(2); O2–Zn3, 2.031(2); O3–Zn1, 1.981(2); O3–Zn3, 2.053(2); O1-Zn1-O3, 94.41(9); O1-Zn2-O2, 94.01(10); O2-Zn3-O3, 97.48(9); and b) the association of dimeric species of $\mathbf{1}_3$ attained through π -stacking interactions.

The central core of **2** consists of a nearly tetrahedral O1 centre (mean Zn-O=1.955 Å, mean Zn-O-Zn= 109.0°) and five zinc centers of a different coordination environment (for a more detailed core structure see the Figure S2, SI).

Two zinc centers, Zn4 and Zn5, coordinated by the oxygen and nitrogen atoms of two quinolinate ligands, and by an O²⁻ ion have an idealized trigonal bipyramid geometry with the ZnNNOO environment. Three other zinc centers have an idealized tetragonal geometry with different enviroments, Zn1 [CZnN(μ -O)(μ_4 -O)], Zn2 [CZn(μ -O)₃], and Zn3 [CZn(μ -O)₂(μ ₄-O)]. The overall shape of this pentanuclear cluster is essentially dictated by both the μ_4 -O coordination mode of the encapsulated oxo anion and the intramolecular π -stacking interactions between the aromatic rings of the quinolinate ligands (yellow dotted lines in Figure 2b). Interestingly, a more detailed analysis of the supramolecular structure of 2 shows that single molecules of 2 utilize their shape to form a set of shifted 1D noncovalently bonded ladder-like chains within a single 2D layer; adjacent ladderlike chains are connected by π -stacking interactions (3.423 Å, green dotted lines in Figure 2b) and are the primary structural directing forces for packing of the sheets. The two-dimensional sheets further pack, through van der Waals (vdW) interactions, into a three-dimensional structure



Figure 2. a) Molecular structure of **2**; hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: O1–Zn1, 1.960(3); O1–Zn2, 1.976(3); O1–Zn4, 1.946(3); O1–Zn5, 1.939(3); Zn1–N1, 1.981(2); Zn4–N2, 2.041(4); Zn4–N3, 2.077(4); Zn5–N4, 2.050(4); Zn5–N5, 2.027(4); Zn1-O1-Zn2, 118.56(14); Zn1-O1-Zn4, 119.15(14); Zn1-O1-Zn5, 113.05(15); Zn2-O1-Zn4, 98.16(13); Zn2-O1-Zn5, 102.82(13); Zn4-O1-Zn5, 102.42(13); and schematic representation of self-assembly processes of single molecules of **2**: b) and c) the intramolecular (*i*) and the intermolecular (*ii*) π – π stacking interactions leading to an extended network with open channels along the *b* axis, d) the space filling graphical representation of the supramolecular architecture.

with a network of one-dimentional channels of 9×7 Å (exluding vdW) that run along the *b* axis and account for 12.5% of the volume of the structure (Figure 2c and d).^[12]

Compound **3** crystallizes in the $P\bar{1}$ space group with four solvated THF molecules, two THFs interacting with the hydroxyl groups by hydrogen bonds (O-H-O distance 2.885 Å) and two THF molecules interacting with the phenolato moieties of the quinoline ligands (Figure 3b). The molecular structure of **3** (Figure 3a) represents a centrosymmetric dimer formed by the association of two dinuclear [Zn(q)₂]-



Figure 3. a) Molecular structure of **3**; hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–O1, 2.006(4); Zn1–O2, 2.025(4); Zn1–O3, 2.053(4); Zn2–O1, 2.091(4); Zn2–O3, 2.094(4); Zn2–N1, 2.136(5); Zn2–N2, 2.153(5); Zn1-O1-Zn2, 99.99(16); Zn1-O2-Zn2, 99.10(16); Zn2-O3-Zn1', 98.64(17); and the crystal structure of **3**: b) 1D noncovalent polymer (with solvated THF molecules) resulting from slight pyridyl–pyridyl ring overlaps between quinoline ligands of neighboring molecules; c) 3D crystal architecture with entrapped THF molecules; d) the space filling graphical representation of 1D open channels.

[*t*BuZn(OH)] moieties comprising the bis-chelate Zn(q₂) and *t*BuZnOH units. The basic skeletal arrangement of **3** can be described as an inversion-related, corner-removed, face-shared cubane, which is a similar structural motif to that observed in the alkylzinc alkylperoxide supported by an O,N-aminealkoxide (*azol*) ligand [EtOOZn(*azol*)]₂[EtZn-(*azol*)]₂ previously reported by us.^[7b] There are two four-coordinate zinc atoms with the terminally Zn-bound *tert*-butyl groups, the CZn(O_{quinolate})₂(O_{hydroxy}) core, and two six-coordinate zinc atoms with peripheral ligation provided by four chelating quinolinate groups. The most striking point of the structure of **3** is the presence of the Zn–OH moiety. The hydroxyl groups act as μ_3 -bridging ligands between the tetrahedral and octahedral zinc atoms with a Zn1–O1 distance of 2.006(4) Å and Zn2–O1 distance of 2.091(4) Å.]

Single molecules of 3 also exhibit intrinsic molecular shape-derived properties for noncovalent-interaction-driven self-assembly into microporous supramolecular architectures (Figure 3b-d). A detailed analysis of the resulting supra-

molecular architecture shows that assembly of molecules of **3** results in the formation of an array of a 1D noncovalent polymer along the *a* axis; adjacent molecules are connected by π -stacking interactions (3.417 Å, green dotted lines in Figure 3b). The polymer chains are close-packed generating a network of quasi-grid 2D layers. The 2D sheets further pack, through van der Waals interactions, into a 3D network with rectangular 1D open channels filled by THF molecules (Figure 3c and d). The average inner diameters of the channels have approximate values of 9×7 Å.

Notably, porous supramolecular architectures are another level of sophistication in the preparation of tailor-made luminescent materials. These materials have recently attracted much interest because of their potential applications in optoelectronic devices or as fluorescent sensors and probes.^[13] Although extensive progress has been made in the development of various luminescent MOFs, reports regarding related noncovalent porous materials are essentially scant. The developed synthesis of a new family of organozinc clusters supported by 8-hydroxyquinolinate ligands opens access to a diverse array of molecular building blocks that can produce novel microporous architectures, and thereby the collaborative functionalities of porosity and luminescence can provide access to novel sensing materials.

Thermogravimetric analysis (TGA) measurements: The thermogravimetric analyses of 1_3 , 2, and 3 were carried out to determine their thermal stability as well as possible pathways of decomposition. The DSC/TGA scans for crystalline 1_3 , 2, and 3 are shown in Figure 4, Figure S5 (in the Support-



Figure 4. Thermogravimetric analysis (TGA, DTG) traces showing the decomposition of compound 1_3 in an inert (Ar) atmosphere.

ing Information), and Figure 5, respectively. Compounds 1_3 and 2 exhibited similar weight loss profiles, in which the first broad decomposition step (in the range of $110^{\circ}C-220^{\circ}C$) with two maxima can be attributed to the partial elimination of *tert*-butyl groups. Further heating above 300°C resulted in the next sharp weight loss step around 360°C leading to a new relatively stable solid up to 600°C. The overall further weight losses for 1_3 and 2 are consistent with zinc oxide for-



Figure 5. Thermogravimetric analysis (TGA, DTG) traces showing the decomposition of compound **3** in an inert (Ar) atmosphere.

mation (see Figures S4 and S5 in the Supporting Information).

Compound 3 exhibited quite a different decomposition profile, which is connected with both the presence of hydroxy groups in the molecular structure as well as THF molecules in the crystal structure. TGA analysis showed that the release of THF molecules from 3 was completed by 90°C with only a 16.2% decrease of weight (calculated theoretical value for 4 THF molecules equals 22.6%). This observation suggests that 1/4 of incorporated THF molecules was evacuated from the crystal structure of 3 by the standard sample preparation procedure (drying under reduced pressure of a vacuum pump; this result is in a good agreement with ¹H NMR spectra and elemental analysis of the studied sample (see the Experimental Section and Figure S12 in the Supporting Information). The next decomposition step with a weight loss of 9.1% and a maximum at 198°C can be attributed to quantitative elimination of isobutane^[7 h] (theoretical value of 9.0%) with the concomitant probable formation of a relatively stable (up to 600 °C) zinc-(oxo)hydroxyquinolinate solid (weight loss of 28.0% and theoretical value of 27.6%). These observations indicate that quinolinate-based organozinc hydroxides are particularly promising precursors of luminescent materials.

Moreover, the powder X-ray diffraction pattern of **3**, after temperature treatment at 90 °C, indicates that the release of THF molecules is accompanied by a transition to a new crystalline phase of unidentified structure (Figure S13 in the Supporting Information). More detailed analysis of the PXRD pattern of **3** after removal of THF indicates a shift of the reflection sequences toward higher angles which suggest a decrease of the unit cell volume by about 20% and contraction of the parent crystal structure. Presumably for this reason, the resulting solid product is essentially nonporous as indicated by the N₂ sorption experiment (BET surface area 4.85 m²g⁻¹; for the N₂ and H₂ adsorption isotherms see Figure S7 in the Supporting Information).

Photoluminescence properties: For determining spectroscopic properties of the resulting complexes the UV/Vis and photoluminescence (PL) measurements of 1_3 , 2, and 3 (including the material derived from the thermal treatment of 3 up to 200 °C) were carried out and the corresponding absorption and emission spectra are shown in Figures 6 and 7



Figure 6. Absorbance (max. at 345 and 380 nm) and photoluminescence (max. at 555 nm) spectra of **3** in toluene; excitation at 380 nm.



Figure 7. Photoluminescence spectra of 1_3 , 2, and 3 measured in toluene indicates the same emission maxima at 555 nm; excitation at 380 nm.

and Figures S8-S10 in the Supporting Information. The absorption and emission maxima for 1_3 , 2, and 3 in toluene are found for the same wavelength (complex absorption bands with two maxima at 345 nm and 380 nm and PL band with maximum at 555 nm) and are close to the reported data for Znq₂ (PL band at 557 nm).^[1b] However, differences in their optical properties in the solid state are observed, which can be explained by various molecular packing characteristics (Figure 8). The emission band of 1_3 in the solid state has a maximum at 555 nm and is redshifted in comparison with the bands of 2 (maximum at 535 nm) and 3 (maximum at 530 nm). Thus, the porous crystal structure of 2 and THFsolvated 3 causes a blueshift of the emission band in comparison with the emission maximum of the close-packed molecular structure of 1_3 . These observations are in line with the recently reported correlations between the molecular density of the packing and the length of interligand contacts



Figure 8. Photoluminescence spectra of 1_3 measured in the solid state (\bullet) with maximum at 555 nm, 2 (\checkmark) with maximum at 535 nm, and 3 (\Box) with maximum at 530 nm; excitation at 350 nm.

of neighboring clusters in crystal structures and the photophysical properties of *mer*-Alq₃ polymorphs (as a consequence of different dispersive and dipolar interactions, as well as different π - π orbital overlaps).^[1c]

Particular attention was paid to determine the photoluminescence properties of the solid materials obtained by the temperature treatment of **3** at points corresponding to the two first temperature transformations (at 90 and 200 °C; see Figure 5). The emission band of **3** heated at 90 °C in the solid state has a maximum at 530 nm and shows no significant changes in comparison to the parent compound. However, the heating of **3** at 200 °C for 1 hour leads to probable formation of zinc(oxo)hydroxyquinolinate solid with different optical properties, that is, an emission maximum at 560 nm (see Figure S11 in the Supporting Information).

Ab initio calculations: DFT calculations were performed for compounds $1_3'$, 2', and 3' in which the *tert*-butyl groups were replaced in the parent compounds by methyl groups. The 3'and 2' molecules are expected to be stable in the gas phase and in the solution. However, the $1_3'$ can in principle dissociate into smaller dimeric or monomeric subunits. To investigate such a possibility we have computed the reaction energies for the dissociation of the trimer into *cis* and *trans* dimers plus a monomer, and into three monomers. It turned out that these reactions are thermodynamically unfavorable, since the energy difference between the substrate and products is strongly negative for all three possible reactions (Figure 9), which is consistent with the experimental data.

We started the comparison between the theoretical and experimental results by analyzing the absorption spectra of $\mathbf{1}_3'$, $\mathbf{2}'$, and $\mathbf{3}'$ in toluene. For $\mathbf{1}_3'$ our calculations predict three bands with wavelengths between 381 and 397 nm. The computed oscillator strengths suggest that mostly one band should be experimentally observed. For $\mathbf{3}'$ we obtained two bands at wavelengths of 392–393 nm and for $\mathbf{2}'$ three bands at wavelengths between 401 and 415 nm. These results are in a quantitative agreement with the experimental results. Indeed, the difference does not exceed a few percent. Such accuracy on the theory side is expected given the size of the



Figure 9. The energy diagram for 1_3 and its possible dissociation subunits *cis*- 1_2 , *trans*- 1_2 , and 1_1 . Energies acquired at PBE0/6-31G++(2p,2d) level of DFT theory.

molecules, especially molecule **2'**. Note that our results do not dramatically depend on the functional used in the calculations.

Different surroundings affect the charge distribution on the zinc atoms. For $1_3'$ and 3' the zinc charges have similar values within the same molecules and are approximately +1.18 and +1.23 *e*, respectively. In the case of the molecule 2', in which the μ_4 -O bridge is formed, the positive charge varies with respect to the zinc atom position. Due to the nature of the alkyl group, charges between +1.28 and +1.32 *e* are assigned to the zinc atoms connected to the alkyl groups, whereas zinc atoms coordinated by the aromatic ligands have higher positive charges, +1.34 and +1.37 *e*, respectively.

Further natural bond analysis of the $\mathbf{1}_3'$, $\mathbf{2}'$, $\mathbf{3}'$ molecules (Figure 10) revealed that the HOMO as well as the LUMO orbitals are localized mostly on the aromatic ligands, which corresponds to the previous investigations for related complexes.^[2b] The frontier orbitals of the $\mathbf{3}'$ molecule are dominated by the s and p type atomic orbitals. For the $\mathbf{2}'$ and $\mathbf{1}_3'$ molecules a similar analysis shows a dominating role of the p-type orbitals, and a similar contribution from the s orbitals in the case of $\mathbf{2}'$ LUMO. HOMO orbitals for $\mathbf{1}_3'$ are mostly

localized on two quinoline ligands, whereas the LUMO is mostly localized on the quinoline ligand on which the HOMO is spread as well. Similarly, the electron density of the 2' HOMO is concentrated mostly on the quinoline ligands. Furthermore, an inspection of the LUMO orbital isodensity plot suggests a possibility of existence of an intramolecular bond. The NBO analysis for 3' reveals extended localization of HOMO and LUMO orbitals on all quinoline ligands. The character of the frontier orbitals, which are not localized on the zinc atom or hydroxyl and alkyl groups, changes from bonding to antibonding when passing from HOMO to LUMO. Moreover, in the case of all of the studied molecules, the electron density of the HOMO is mostly concentrated on the phenolato ring. By contrast, electron distribution affects the pyridyl groups for all LUMO orbitals, which is consistent with a similar calculation for Znq₂ and (Znq₂)₂.^[2b] It seems that the HOMO/LUMO electron density concentration on the quinoline ligands can result in changes to the electronic properties due to the nature of the intermolecular interactions, which has been explored in our X-ray section. We also performed calculations (PBE0/6-31G + +(2p,2d)) for $1_3'$, 2', and 3' to compare HOMO/ LUMO values for $1_3'$, 2', and 3' as well as for homoleptic Znq₂ and (Znq₂)₂ complexes (as the representatives of the zinc quinoline complexes family). The HOMO/LUMO gaps for $\mathbf{1}_{\mathbf{3}}'$, $\mathbf{2}'$, and $\mathbf{3}'$ have values between 3.73 and 3.94 eV, whereas for Znq_2 and $(Znq_2)_2$ we found the corresponding values of 3.80 and 3.49 eV, respectively.

Conclusion

We have successfully synthesized and characterized novel organozinc 8-hydroxyquinolinate complexes as precursors of potential new materials for luminescence applications. The existence of the reactive Zn–C bond in the reported complexes is a unique feature qualifying these systems for further post-synthetic modifications to enhance the stability or tune the desired luminescence properties. Strikingly, the



Figure 10. HOMO (a, b, and c) and LUMO (a', b', and c') computed for 13', 2', and 3', respectively.

study demonstrates that alkylzinc 8-hydroxyquinolinate complexes upon reaction with H₂O can be efficiently transformed to the corresponding oxo- and hydroxozinc clusters supported by the quinoline ligands. Moreover, these novel molecular aggregates exhibit an intriguing high propensity for the formation of microporous solids resulting from noncovalent-interaction-driven self-assembly. The collaborative functionalities of porosity and luminescence are features that enabled the described luminescent compounds to be a very promising new

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type of sensing materials. The presented approach appears as an emerging strategy for the design and construction of new luminescent materials based on 8-hydroxyquinoline derivatives.

Experimental Section

Methods and materials: All experiments and manipulations were carried out under a nitrogen atmosphere. Reactions were performed by using standard Schlenk techniques and in thoroughly dried deoxygenated solvents. The NMR data were obtained on a Varian Mercury (400MHZ) spectrometer in [D₆]benzene or [D₈]THF solution at room temperature. The infrared spectra were recorded on a FTIR PerkinElmer System 2000 spectrometer. Samples were prepared as a suspension of the analyzed compounds in nujol. Thermogravimetric experiments were performed in argon with a heating rate of 2°C min⁻¹ using a TA Instruments Q600 apparatus. BET surface area (m²g⁻¹) measurements were collected at 77 K by dinitrogen on an ASAP 2020. The absorption measurements were carried out using a Shimadzu UV3100 spectrophotometer. Powder X-ray diffraction (PXRD) data for compound were collected on a BRUKER D8 ADVANCE diffractometer using $Cu_{K\alpha}$ radiation. The luminescence spectra were recorded on Hitachi F-7000 spectrophotometer. The structures were solved by direct methods with the SHELXS-97 program and were refined by full matrix least squares F^2 by using the program SHELXL-97. H-atoms were included in idealized positions and refined isotropically.

Synthesis and characterization:

[(tBu)Zn(q)]₃ (1₃): tBu₂Zn (0.50 mL, 0.69 mmol, 1.39 M in toluene) was treated with the dried 8-hydroxyquinoline (0.100 g, 0.69 mmol) dissolved in toluene (2 mL) at -78 °C and the resultant suspension was allowed to warm to room temperature. The suspension was stirred at room temperature for a few minutes until complete dissolution of the particles. Afterwards 10 mL of hexane was added and large yellow crystals of 1 were deposited after crystallization at -25 °C (isolated yield 0.158 g, 86%). ¹H NMR (C_6D_6): $\delta = 8.22$ (brm, 1H; 2-CH), 7.40 (brm, 1H; 7-CH), 7.35 (brm, 1H; 3-CH), 7.11 (brm, 1H; 6-CH), 6.64 (brm, 1H; 5-CH), 6.54 (brm, 1H; 4-CH), 1.40 ppm (brs, 9H; C(CH₃)₃); IR: $\tilde{\nu}$ =2920 (m), 2860 (m), 2812 (s), 2752 (w), 2696 (w), 1600 (s), 1577 (s), 1497 (vs), 1464 (vs), 1377 (vs), 1316 (s), 1270 (s), 1237 (s), 1104 (s), 820 (s), 781 (s), 729 (s), 643 cm⁻¹ (m); elemental analysis calcd (%) for $C_{39}H_{45}N_3O_3Zn_3$ (799.95 gmol⁻¹): C 58.50, H 5.63, N 5.25, O 6.00; found: C 58.93, H 5.65, N 5.23, O 5.91. In benzene solution, equilibrium agglomeration of complex 1 is 2.69.

[(*t***Bu)₃Zn₅(μ₄-O)(q)₅] (2)**: *t*Bu₂Zn (0.45 mL, 0.6 mmol, 1.36 м in toluene) was treated with commercial grade 8-hydroxyquinoline (0.087 g, 0.6 mmol) dissolved in toluene (3 mL) at -78 °C and the resultant suspension was allowed to warm to room temperature. The suspension was stirred at room temperature for a few minutes until complete dissolution of the particles. Afterwards 10 mL of hexane was added and large yellow crystals of 2 were deposited after crystallization at 4°C (isolated yield 0.061 g, 41%). ¹H NMR (C₆D₆): δ = 8.73 (brm, 2H; Ar), 8.27 (brm, 1H; Ar), 8.09 (m, 1H; Ar), 7.50 (brm, 13H; Ar), 7.01 (m, 2H; Ar), 6.79 (brm, 6H; Ar). 6.36 (brm, 5H; Ar), 1.90 (s, 1H; C(CH₃)₃), 1.76 (m, 1H; C(CH₃)₃), 1.67 (m, 4H; C(CH₃)₃), 1.43 (s, 3H; C(CH₃)₃), 1.22 (brm, 4H; $C(CH_3)_3$, 0.88 (t, J(H-H) = 7.2 Hz, 1H; $C(CH_3)_3$), 0.68 (s, 2H; $C(CH_3)_3$), 0.62 (s, 1H; C(CH₃)₃), 0.29 ppm (s, 1H; C(CH₃)₃); IR: 2916 (m), 2808 (s), 2724 (w), 2682 (w), 1601 (m), 1574 (s), 1498 (vs), 1463 (vs), 1377 (vs), 1317 (s), 1270 (s), 1237 (s), 1104 (s), 819 (s), 780 (s), 729 (s), 642 cm⁻ (m); elemental analysis calcd (%) for $C_{57}H_{57}N_5O_6Zn_5$ (1235.03 gmol⁻¹): C 55.38, H 4.62, N 5.67, O 7.77; found: C 55.48, H 4.70, N 5.62, O 7.65.

 $[Zn(q)_2]_2[tBuZn(OH)]_2(4THF)$ (3-4THF): tBu_2Zn (0.50 mL, 0.68 mmol, 1.36 M in toluene) was treated with water (6 µL, 0.34 mmol) and dried 8-hydroxyquinoline (0.100 g, 0.68 mmol) dissolved in toluene (3 mL) at -78 °C. The resultant solution was allowed to warm to room temperature and mixed for an additional 10 h. The solid residue, obtained after removal of the solvent under reduced pressure, was recrystallized from

THF/hexane solvents mixture. Large yellow crystals of **3** deposited after a few days at room temperature (isolated yield 0.171 g, 79%). ¹H NMR ([D₈]THF): δ =8.35 (m, 1H; Ar), 8.09 (brm, 1H; Ar), 7.39 (brm, 1H; Ar), 7.23 (m, 1H; Ar), 7.15 (brm, 1H; Ar), 6.94 (brm, 1H; Ar), 3.22 (s, 1H; OH), 1.39 ppm (m, 9H; C(CH₃)₃); IR: 3530 (s), 3053 (s), 2978 (s), 2869 (s), 2272 (w), 1604 (s), 1579 (s), 1497 (s), 1465 (s), 1388 (s), 1326 (s), 1239 (m), 1194 (m), 1110 (s), 1063 (s), 909 (m), 824 (s), 657 (m), 616 CM⁻¹ (m); elemental analysis calcd (%) for C₄₄H₄₄N₄O₆Zn₄·4-(C₄H₈O): (1274.81 gmol⁻¹):C 56.48, H 5.96, N 4.39, O 12.56; found: C 52.13, H 5.53, N 4.31, O 7.55.

Crystallographic data: The data were collected at 100(2) K on a Nonius Kappa CCD diffractometer^[14] using graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The crystal was mounted in a nylon loop in a drop of silicon oil to prevent the possibility of decay of the crystal during data collection. The unit cell parameters were determined from ten frames and then refined on all data. The data were processed with DENZO and SCALEPACK (HKL2000 package)^[15]. The structure was solved by direct methods using the SHELXS97^[16] program and was refined by full matrix least-squares on F² using the program SHELXL97.^[17] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.5 (methyl groups) times the value of the equivalent isotropic displacement parameter of the parent carbon. CCDC-832770 (13), CCDC-832771 (2), and CCDC-832772 (3) contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data request/cif. For selected bond distances see Tables S1, S2, and S3 in the Supporting Information.

Crystal data for 1₃: $C_{39}H_{45}N_3O_3Zn_3$: M = 799.95; monoclinic; space group $P \ 21/c$ (no. 14); a = 12.2341(3), b = b = 19.2112(5), c = 16.4101(3) Å; $\beta = 98.807(2)^\circ$; U = 3811.33(15) Å³; Z = 4; F(000) = 1656; $\rho_{cald} = 1.394$ gm³; μ -(Mo_{Ka}) = 1.08 mm⁻¹; $\theta_{max} = 24.71^\circ$; 5102 unique reflections; R1 = 0.0404; wR2 = 0.0985 for 5709 reflections with $I_o > 2\sigma(I_o)$. The goodness-of-fit on F² was equal to 1.086.

Crystal data for 2: $C_{57}H_{57}N_5O_6Zn_5$: M = 1235.03; triclinic; space group $P\bar{1}$ (no. 2); a = 11.6329(5), b = 12.4501(6), c = 21.7511(9) Å; $\alpha = 92.754(2)$, $\beta = 101.111(2)$, $\gamma = 108.370(2)^\circ$; U = 2913.6(2) Å³; Z = 2; F(000) = 1264; $\rho_{cald} = 1.408 \text{ gm}^3$; $\mu(Mo_{Ka}) = 2.079 \text{ mm}^{-1}$; $\theta_{max} = 24.71^\circ$; 9605 unique reflections; R1 = 0.0457; wR2 = 0.1024 for 8063 reflections with $I_o > 2\sigma(I_o)$. The goodness-of-fit on F² was equal to 1.037.

Crystal data for 3: C₄₄H₄₄N₄O₆Zn₄·4(C₄H₈O): M = 1274.81; triclinic; space group $P\bar{1}$ (no. 2); a = 11.6248(7), b = 12.1339(5), c = 12.7951(8) Å; $\alpha = 83.798(4)$, $\beta = 65.470(2)$, $\gamma = 65.910(3)^{\circ}$; U = 1494.80(15) Å³; Z = 1; F = (000) = 664; $\rho_{cald} = 1.416$ gm³; T = 100(2) K; $\mu(Mo_{Ka}) = 1.644$ mm⁻¹; $\theta_{max} = 25.73^{\circ}$; 5348 unique reflections; R1 = 0.0671; wR2 = 0.1298 for 3752 reflections with $I_o > 2\sigma(I_o)$. The goodness-of-fit on F² was equal to 1.083.

Theoretical details: Geometries of the 1, 2, and 3 molecules were optimized by using the density functional theory (DFT) with the $\ensuremath{\text{PBE0}}^{[18]}$ and M062x^[19] functionals in the 6-31 + +G(2p,2d) basis set. Frequency calculations were done to confirm that the optimal geometry corresponds to the minimum on the potential energy surface and to get the zero-point energies (ZPE). Vertical excitation energies for transitions from the ground to the first excited state that is electric dipole allowed were computed with the time-dependent density functional theory (TDDFT). The geometries of the excited states of the molecules were not optimized. Although such a procedure is now available at the TDDFT level, it would be very time-consuming for molecules of that size. Finally, the natural bond analysis (NBO)^[20] of the ground state orbitals was used to determine the molecular electron densities and to elucidate the origins of the bonding. The largest molecule considered in the present paper (2) has 560 electrons, and its theoretical description in the 6-31 + +G(2p,2d)basis would require 2136 basis functions. To simplify the computational task we have replaced the tert-butyl groups with methyl groups. Finally, the solvent effects were neglected in our calculations. We have found however, using an example of the monomer tBuZn(q), that toluene as the solvent does not introduce any major changes in the excitation ener-

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gies, at least within the PCM continuum model of the solvent. All calculations were done with the Gaussian09 suite of codes. $\ensuremath{^{[21]}}$

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