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Improved Access to 1,8-Diformyl-carbazoles Leads to Metal-Free Carbazole-Based [2 + 2] Schiff Base Macrocycles with Strong Turn-On Fluorescence Sensing of Zinc(II) Ions

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Supporting Information

ABSTRACT: Development of a new and high yielding synthetic route to 1,8-diformyl-carbazoles **3** (**3a** 3,6-di-*tert*-butyl substituted; **3b** 3,6-unsubstituted) is reported. Use of a Heck coupling reaction, followed by ozonolysis, has greatly facilitated the preparation of these interesting head units in useful quantities. An initial foray into the new generations of Schiff base macrocycles that ready access to these head units



(3) opens up, has led to the direct (i.e., metal-free) synthesis of two [2 + 2] macrocycles from **3a** or **3b** with 1,2-diaminoethane, H_2L^{tBu} (**4a**) and H_2L^{H} (**4b**), respectively, obtained as yellow powders in high yields (87–88%). The dizinc complex $[Zn_2L^{H}(OAc)_2]$ (**5b**) was isolated as a bright yellow solid in 83% yield, by 1:2:2 reaction of H_2L^{H} with zinc(II) acetate and triethylamine. Aldehydes **3a** and **3b**, macrocycle H_2L^{H} , and complex $[Zn_2L^{H}(OAc)_2]$ (**5b**) have been structurally characterized. The carbazole NH makes bifurcated hydrogen bonds with the pair of flanking 1,8-diformyl-moieties in **3**, or 1,8-diimine-moieties in H_2L^{H} leading to a flat, all-*cis* conformation. The stepped conformation of the metal-free macrocycle H_2L^{H} is retained in $[Zn_2L^{H}(OAc)_2]$, despite deprotonation and binding of two zinc(II) centers within the two tridentate pockets. The N_3O_2 coordination of the zinc ions is completed by one $\mu_{1,1^-}$ and one $\mu_{1,3^-}$ bridging acetate anion. Excitation of nanomolar $[Zn_2L^{H}(OAc)_2]$ in DMF at 335 nm results in clearly visible blue fluorescence ($\lambda_{max} = 460$ nm). Further studies on the H_2L^{H} macrocycle revealed turn-on fluorescence, with selectivity (over Ca²⁺, Mg²⁺ and a range of 3d dications) and nanomolar sensitivity for zinc(II) ions, highlighting one of the many potential applications for these new carbazole-based Schiff base macrocycles.

INTRODUCTION

Macrocycles are a very powerful class of ligand, not least due to the control they exhibit over the coordination environment of the metal ion(s).^{1–8} Schiff base macrocycles are a popular class of macrocycles, as they can be readily accessed by the metal templated condensation of dialdehyde or diketone (head unit) and diamine (linker) components.^{9–11} Head units featuring, for example, pyridine, phenol, pyridazine, pyrrole, dipyrrole, triazole, dihydroxybenzene, and diphenylamine moieties have been utilized to form Schiff base macrocyclic complexes that have a wide range of applications, for example, as hydrogen evolution catalysts,^{12–14} carbon dioxide reduction catalysts,¹⁵ CO_2 /epoxide copolymerization catalysts,¹⁶ spin crossover switches,^{17,18} single molecule magnets,^{19,20} antimicrobials,¹¹ metalloenzyme models,^{21–23} nuclear waste remediation,²⁴ and DNA binding agents.^{25,26}

We have a long-standing interest in Schiff base macrocycles utilizing diphenylamine-based systems,²⁷ for example, to (a) generate redox active complexes,²⁸ (b) fine-tune the spin states of nickel(II),²⁹ and (c) generate hyperactive catalysts for the ring-opening polymerization of lactide into polylactide.^{16,30,31} In looking to develop the next generation of related Schiff base macrocycles, we identified in a recent literature review that there were *no Schiff base macrocyclic systems based on 1,8-*

diformyl-carbazole head units,²⁷ until our report in 2017.³² Prior to our paper, only a small set of complexes of *acyclic* 1,8diimino-carbazole ligands had been reported.^{33–36} The key 1,8diformyl-carbazoles (**3**), required for accessing these Schiff base macrocyclic and acyclic ligands, were prepared using three very different routes, reported by the groups of Gibson,^{33,34} Nakagawa,³⁷ and Brown/Brooker^{32,38} (Scheme 1). Deprotonation of the resulting tridentate 1,8-diimino-carbazole ligands facilitated complexation with manganese(II), iron(II or III), cobalt(II), nickel(II), copper(II), or palladium(II).

However, the three routes reported to date to the key 1,8diformyl-carbazole head units **3** (Scheme 1)^{32–34,38} are nontrivial^{32,38} or hazardous,^{33,34} and time-consuming, and so had severely limited our access to systems derived from them.^{32,33}

Herein, we describe a new and reliable route that facilitates the larger scale preparation of 3, which in turn opens up the exploration of ligands and complexes derived from it. Specifically, we report here the preparation of the first examples²⁷ of [2 + 2] Schiff base *macrocycles* to be derived from these carbazole head units. The metal-free condensation

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^{*a*}The new route reported herein is shown in Scheme 2.

of the **3a** (3,6-di-*tert*-butyl substituted) or **3b** (3,6-unsubstituted) 1,8-diformyl-carbazoles with 1,2-diaminoethane generates two [2 + 2] macrocycles, H_2L^{tBu} and H_2L^{H} , respectively (Scheme 2), which show selective and strong turn-on fluorescence in the presence of zinc(II) ions. Indeed, H_2L^{H} shows potential as a *competitively selective, sensitive* and *strong turn-on blue fluorescence* sensor of zinc(II) ions, highlighting one of the many new and exciting applications that we hope to access through this new family of carbazole-based Schiff base macrocycles.

RESULTS AND DISCUSSION

Synthesis of 1,8-Diformyl-carbazoles (3). Previous work with 1,8-diformyl-carbazole head units 3 has relied on the use of two different, but nontrivial, time-consuming and scale limiting synthetic routes to access them (Scheme 1); hence, very few such studies have been reported to date.^{32–34,38} To alleviate this problem, a new synthetic route starting from known 1,8-dibromo-carbazoles 1 was devised, in which they are converted into the desired 1,8-diformyl-carbazoles 3 by means of a Heck coupling, followed by ozonolysis (Scheme 2). We illustrate this approach here, with the preparation of two such 1,8-diformyl-carbazoles, 3,6-di-*tert*-butyl substituted **3a** and 3,6-unsubstituted **3b**.

The two 1,8-dibromo-carbazole starting materials employed here, 3,6-di-*tert*-butyl-1,8-dibromo-carbazole³⁹ **1a** and 1,8-dibromo-carbazole⁴⁰ **1b**, are both literature compounds. However, the reported synthesis of **1b** involved multiple steps from carbazole and had a low overall yield, so an alternative route is employed here. Specifically, 3,6-di-*tert*-butyl-

Scheme 2. New Route to 1,8-Diformyl-carbazoles 3a (R = tBu) and 3b (R = H) and the Subsequent Direct Synthesis of Two Metal-Free [2 + 2] Schiff Base Macrocycles, H_2L^{tBu} and H_1L^H



1,8-dibromo-carbazole **1a** was converted into 1,8-dibromocarbazole **1b**, in one step in good yield (70%) and short reaction time, using a reverse Friedel crafts reaction (the protocol used is based on a related literature transformation⁴¹).

These two 1,8-dibromo-carbazoles 1 are then reacted with styrene in a Heck coupling, under an atmosphere of $N_{2^{j}}$ using a palladium catalyst, to access the 1,8-distyryl-carbazoles 2. Considerable optimization of this reaction led to identification of the best conditions: a solvothermal reaction of a suspension of the reagents in a small volume of THF and triethylamine, sealed in a Teflon tube inside a steel pressure vessel and heated to well beyond the boiling point of THF. This produced both 1,8-distyryl-carbazoles 2 in greater than 70% yield and was scalable (>2 g per 50 mL pressure vessel).

Synthesis of these two distyryl compounds (2) places double bonds in the positions required in order to access the required dialdehydes by ozonolysis, a route that we and others had successfully taken to access another interesting head unit, 3,6diformylpyridazine.^{42,43} A DCM solution of the respective 1,8distyryl-carbazole, at -78 °C, was bubbled with O_3/O_2 (*Caution!*) for about 5 min (until blue-green color indicates saturation by ozone), then purged with N_2 before being quenched with dimethyl sulfide. After warming the solution to room temperature, the solvent was removed and column chromatography used to purify the solid. The desired 1,8diformyl-carbazoles **3a** and **3b** were obtained as bright yellow and orange-yellow solids, respectively, in good to high yields 70–90% (see the SI, Figures S1–S8 for ¹H NMR spectra of all compounds reported in this paper).

Crystal Structures of 1,8-Diformyl-carbazoles 3a and 3b. Single crystals of both dialdehydes were grown by slow evaporation of chloroform solutions and were analyzed by X-ray diffraction (Figure 1; also see the SI, Table S1 and Figures S9–S12 for all crystallographic details). Both contain the whole molecule in the asymmetric unit, with both of the aldehyde



Figure 1. Crystal structures of 3b (left) and $3a \cdot CHCl_3$ (right; solvent of crystallization not shown). Thermal ellipsoids drawn at 50% probability.

oxygen atoms (O1/O2) facing inward and hydrogen bonding to the amine proton (N1-H) of the carbazole head unit.

Synthesis of [2 + 2] Schiff Base Macrocycles. With these key aldehydes, 3, now readily available in large quantities, forming a wide range of metal-free Schiff base macrocycles (and noncyclic ligands) from them is being actively explored,^{32,44} and the first examples of [2 + 2] macrocycles are presented herein.

The direct, i.e., metal-free, synthesis of macrocycles from a dialdehyde head unit and diamine lateral component is usually challenging, as a variety of different sized macrocycles as well as oligomeric materials are possible. Added to this, Schiff base macrocycles are not always stable metal-free. However, the direct synthesis of both [1 + 1] and [2 + 2] Schiff base macrocycles was successful for the analogous diphenylamine head units,^{28,30,45} as well as for [1 + 1] Schiff base carbazole macrocycles,³² so it was attempted here also.

Condensation of a 1:1 ratio of the head unit, **3a** or **3b**, and 1,2-ethylene diamine in a small volume of refluxing ethanol proved successful, with the [2 + 2] macrocycles precipitating on formation. The precipitate also included a small amount of insoluble material, likely to be polymeric in nature, which could be easily removed after dissolving the macrocycle in chloroform, then simply filtering to remove the byproduct. This worked exceedingly well for both **3a** and **3b**, with the respective [2 + 2] macrocycles, H_2L^{tBu} and H_2L^{H} , obtained as analytically pure pale yellow solids in yields of >80%.

Crystal Structure of H_2L^H. Single crystals of the macrocyclic ligand H_2L^H were grown by diethyl ether vapor diffusion into a 1:1 chloroform:ethanol solution of the compound and analyzed by X-ray diffraction (Figure 2; also the SI, Table S1, Figures S9 and S10). The asymmetric unit for this structure is



Figure 2. Crystal structure of H_2L^{H} ; symmetry operation A is 1 - x, 1 - y, 1 - z. Thermal ellipsoids drawn at 50% probability.

half of the overall molecule. The structure shows the two rigid head units of the macrocycle, with the planes of the two head units running parallel. The pair of imine nitrogen atoms (N2 and N3A; N2A and N3) face in toward the proton (H1; H1A) of the carbazole amine between them due to forming a bifurcated hydrogen bond (Figure 2).

Synthesis of Dizinc(II) Complex 5b. The neutral dizinc complex $[Zn_2L^H(OAc)_2]$ (5b) was prepared by reaction of the metal-free macrocycle H_2L^H with 2 equiv of zinc(II) acetate and 2 equiv of triethylamine in refluxing CHCl₃:MeOH (1:1). The product was isolated as an analytically pure bright yellow solid by removing the solvents, washing the crude solid with ice-cold methanol, and filtering.

As zinc(II) is diamagnetic, the ¹H NMR spectrum of $[Zn_2L^{H}(OAc)_2]$ was obtained, in CDCl₃ as it is highly soluble in this solvent (Figure S8). This confirms the loss of the NH proton. It also reveals a slight upfield shift in the imine proton signal in the zinc complex relative to that seen for H_2L^{H} , and that the 8 alkyl linker CH₂ hydrogen atoms appear as two 4H doublets in the complex, whereas they were a single singlet (all equivalent) in H_2L^{H} . The latter observation, that the 8H singlet resolves as two 4H peaks, is because there is now one signal for each position in space of the two CH₂ protons, either up or down, relative to the 1,3 acetate bridge (see later, Figure 3).



Figure 3. Crystal structure of $[Zn_2L^H(OAc)_2]$, hydrogen atoms removed for clarity; symmetry operation A is 1 - x, 1 - y, 1 - z. Thermal ellipsoids drawn at 50% probability.

The cryospray mass spectrum shows a major peak at 655.0750 m/z corresponding to $[Zn_2L^H(Cl)]^+$, confirming the presence of the dizinc [2 + 2] Schiff base macrocyclic core (adventitious chloride obtained from surroundings). The complex was also characterized by microanalysis, UV–vis spectroscopy (Figure S13), and X-ray crystallography (see the Experimental Section and the SI for characterization details).

Crystal Structure of Dizinc(II) Complex 5b. Single crystals of $[Zn_2L^H(OAc)_2]$ (**5b**) are grown by slow cooling of the reaction solution (see the SI, Figure S9). This neutral complex crystallized with half the molecule in the asymmetric unit and the other half generated by inversion. Hence, both of the bridging acetate anions are disordered by symmetry over two sites (50:50): one forms a 1,3-bridge and the other a 1,1-bridge (Figure 3; also the SI, Figure S11).

The structure confirms that loss of the carbazole amine protons (N1-H) generates two tridentate pockets that bind the two zinc(II) centers. Each zinc(II) center has an N₃O₂ donor set, but due to the acetate disorder, one of them is square pyramidal ($\tau = 0.08$) while the other is closer to trigonal bipyramidal ($\tau = 0.59$). Note $\tau = 0$ for a square pyramid versus 1 for a trigonal bipyramid.⁴⁶ The macrocycle conformation in this complex is almost identical to that of the free macrocycle,

with only a slight variation in the alkyl chain conformations in order to accommodate the pair of, $\mu_{1,1}$ - and $\mu_{1,3}$ -acetate bridged, zinc(II) centers (SI, Figures S11 and S12).

Fluorescence Testing. Zinc ions are essential to life and play a wide range of roles throughout biology, so the development of chemosensors capable of visualizing them by, preferably "turn-on", fluorescence has been the subject of considerable activity.⁴⁷⁻⁵¹ Recent work into sensing zinc ions by chelation enhancement of fluorescence has utilized both acvclic⁵²⁻⁵⁷ and macrocyclic⁵⁸⁻⁶¹ ligands as probes. Macrocyclic probes, such as well-known Robson and corrole macrocycles, are favored due to stabilization of the resulting complex by the macrocyclic effect. In the case of such *chelating* agents, the incorporated fluorophore is often a large area of aromatic conjugation, with a couple of examples of Schiff base chemistry being employed to extend the conjugation through the imine double bond as well as provide a donor atom for binding the zinc ion. 52,62-64 In the other class, the fluoroionophores, one of the under-utilized fluorophores is carbazole,^{65,66} which has been widely utilized in other areas of chemistry due to its excellent photophysical properties.⁶⁷

Hence, the observation of strong blue fluorescence by the isolated dizinc carbazole complex **5b** when irradiated with 335 nm light (Figure 4) prompted testing of the two macrocycles as



Figure 4. UV–vis spectra of H_2L^H (dotted blue) and $[Zn_2L^H(OAc)_2]$ (dotted red) in DMF (left axis, dotted curves) and the fluorescence spectra, 350–600 nm, of H_2L^H with 4 equiv of zinc(II) (blue) and $[Zn_2L^H(OAc)_2]$ (red), irradiated at 335 nm (right axis, solid curves).

potential turn-on fluorescence chemosensors for zinc(II) ions. Initial tests of 1.1×10^{-9} mol L⁻¹ DMF solutions (DMF was chosen as it was found to be the only solvent in which both the macrocycle and metal salts were soluble) of each of the two macrocycles with 4 equiv of zinc(II) acetate (no additional base), exciting at 335 nm, resulted in strong turn-on blue fluorescence, with a slight shift in λ_{max} (510 nm) compared to the dizinc complex (460 nm). Both *visual and analytical detection of zinc(II) ions* is possible at *nanomolar concentrations*. H₂L^H gave a more intense fluorescence (40.24 a.u.) than H₂L^{EBu} (6.44 a.u.; see Figure S14), so only the stronger sensor, the H₂L^H macrocycle, was tested further.

The fluorescence intensity at 510 nm was monitored as the amount of zinc(II) acetate added to a DMF solution of H_2L^H was increased from 0 to 10 equiv. From 0 to 4 equiv of zinc(II), the fluorescence intensity increased linearly, after which the addition of further equivalents of zinc(II) produced no significant change (Figures S15 and S16). This is consistent with the tetra-imine macrocycle interacting with one zinc(II) ion per imine nitrogen atom, under these conditions (no added

base). In general, the zinc-induced fluorescence of Schiff base macrocycles is proposed to be due to the chelated-enhanced fluorescence effect (CHEF), an effect that zinc is particularly good at inducing (whereas heavy metal ions and paramagnetic metal ions usually do not).^{71–73} In the present case, it is likely that the zinc(II) ions are binding to the lone pairs of electrons of the imine nitrogen atoms which were previously blocking the photoinduced electron-transfer effect (PET),⁷⁴ allowing fluorescence to occur.

This result, of four zinc ions interacting with each macrocycle, was interesting as it had been expected that only two zinc(II) ions would do so, by coordinating in the binding pockets of the macrocycle in the manner seen for the isolated dizinc complex (Figure 3). To probe this result further, a ¹H NMR titration study in *d*-DMF was undertaken, looking at solutions of (a) H_2L^H , (b) H_2L^H with 2 equiv of zinc(II) acetate, (c) H_2L^H with 4 equiv of zinc(II) acetate, and (d) the isolated dizinc complex 5b (see Figures S17-S21). This study was limited by the very poor solubility of the macrocycle in DMF (the only solvent that both the macrocycle and metal salts dissolved in), with long ¹H NMR acquisition times (hours) required. Nevertheless, the ¹H NMR spectra of these solutions are informative. In particular, for the solutions containing 2 or 4 equiv of $Zn(OAc)_2$ with H_2L^H , (a) there is almost no difference between the spectra, (b) while broad, an NH proton signal is seen, and (c) a minor species of apparently lower symmetry is also seen in both of those spectra (Figures S19 and S20). Finally, the peaks of the major species in those two solutions were almost identical to those observed for the isolated dizinc complex 5b.

To further probe the role of the acetate anion in the formation of the 4:1 Zn to H_2L^H species (maximum fluorescence, Figures S15 and S16), the fluorescence titration study was repeated with zinc(II) *tetrafluoroborate* (Figure S22). This reveals interesting changes in behavior, with (a) the initial 0.4 equiv of zinc(II) tetrafluoroborate gave a much larger percentage of the maximum fluorescence intensity (at $\lambda_{max} = 470 \text{ nm}$) compared to the zinc(II) acetate titration, and (b) the maximum fluorescence intensity of or only 2 equiv of zinc(II) tetrafluoroborate (see Figures S16, S22, and S23). These results are consistent with the acetate anion playing a key role in the formation of the 4:1 species with H_2L^H in solution, probably by coordination to zinc(II), which tetrafluoroborate is unlikely to do instead, hence leading to the observed 2:1 species in that case.

The earlier fluorescent testing with zinc(II) acetate was performed without added base. In contrast, 2 equiv of triethylamine was added to prepare the structurally characterized dizinc complex $[Zn_2L^H(OAc)_2]$, in which the carbazole N-H groups have been deprotonated, facilitating binding of two zinc(II) ions in the resulting pair of tridentate pockets of the macrocycle (Figure 3; also the SI, Figure S11). For completeness, 2 equiv of zinc(II) acetate was added to a DMF solution of $[Zn_2L^H(OAc)_2]$: this does not alter the fluorescent response (λ_{max} 460 nm, Figure S24).

As deprotonation of carbazole can be slow,³³ the effect of added base was probed in more detail, over time, as follows. To a DMF solution that contained 2 equiv of zinc(II) acetate per H_2L^H was added 2 equiv of base (triethylamine), and the fluorescence spectra were monitored over the subsequent 9 h (Figures S25 and S26; after 9 h, the macrocycle started to break down and therefore fluorescence was lost). The increase in intensity of the peak at 460 nm over time after base addition

reflects the macrocycle deprotonating and forming a dizinc complex (Figure S27). Clearly, the macrocycle still functions as an effective fluorescent zinc sensor under basic conditions, with only a shift in λ_{max} and change in maximum equivalents of zinc to allow for if quantification is required.

 H_2L^H was then tested against a range of other first row transition metal(II) ions, as well as the most common biological dications, calcium and magnesium (Figures 5 and 6). The



Figure 5. A series of 2.0×10^{-7} mol L⁻¹ DMF solutions of H₂L^H and M²⁺, above in natural light and below under 366 nm light.



Figure 6. Competitive binding studies of 6.8×10^{-9} mol L⁻¹ H₂L^H in DMF, with 4.6 equiv of both Zn(OAc)₂ and M(OAc)₂ (M = Ca, Mg, Mn to Cu), $\lambda_{ex} = 335$ nm, $\lambda_{em} = 510$ nm.

results show excellent *fluorescent selectivity for zinc(II)*, with at least 5 times greater emission signal for zinc(II) at $\lambda_{max} = 510$ nm than for any of the other transition metal(II) ions. The next strongest fluorescence signals came from the two biologically relevant dications, calcium and magnesium, but these were still weak relative to that of zinc.

Competition studies, using 1:4:4 mixtures of macrocycle:zinc-(II) ion:other metal(II) ion, were employed to further test the selectivity of H_2L^H for zinc(II) ions (Figure 6). The macrocycle clearly strongly favors interacting with zinc(II) ions over the other first row transition metal(II) ions: only cobalt(II) and copper(II) ions compete to some extent with the zinc(II) ions, as shown by a slightly lower fluorescence intensity than is observed when only zinc(II) is present. The result of the copper(II) experiment is particularly interesting as copper(II) ions are expected to have a stronger binding affinity than zinc(II) ions according to the Irving–Williams series.

CONCLUSION

Key 1,8-diformyl-carbazole compounds (3a and 3b) have been synthesized in reliable, high yielding, and scalable reactions

through the design and application of a new synthetic route. This breakthrough enables ready access to larger quantities of 3 which really opens up the development of exciting new generations of carbazole-based Schiff base ligands and complexes, which have potential applications in catalysis, redox, photophysics, and sensing applications. Herein, this potential is illustrated by the synthesis of two metal-free [2 + 2]macrocycles, H_2L^H and H_2L^{tBu} , and a strongly blue fluorescent dizinc macrocyclic complex, $[Zn_2L^H(OAc)_2]$ ($\lambda_{max} = 460$ nm). Subsequent fluorescence studies showed that the $H_2 L^H$ macrocycle produces intense turn-on blue fluorescence in the presence of zinc(II) ions at very low, nanomolar, concentrations. In competitive studies, H_2L^H also shows strong selectivity for zinc(II) ions over other first row transition metal(II) ions (Mn-Cu) as well as other biologically relevant metal(II) ions (Ca and Mg). Testing the H₂L^H macrocycle with added base showed retention of the blue fluorescence, but with a decrease in the λ_{max} toward that of the isolated dizinc complex. These fluorescence results are very promising, but clearly the solubility of the system needs to be improved significantly, preferably to allow testing in water (rather than being limited to DMF as at present). However, a wary eye will also need to be kept open to the stability of the system in such solvents. The increased solubility in water may be achievable by appropriate choice of R substituents, such as polyethylene glycol (PEG) "tails", at the 3- and 6-positions of the carbazole rings. In summary, this new synthetic route to 1,8-diformylcarbazoles (3) has unlocked the door to the synthesis of many exciting new carbazole-based Schiff base macrocycles and complexes.

EXPERIMENTAL SECTION

Chemicals were used as received, including $PdCl_2(PPh_3)_2$ and dimethylsulfide (DMS), except for the following: 3,6-di-*tert*-butyl-1,8-dibromo-carbazole was prepared according to the literature method,³⁹ and NBS was recrystallized from water before use. Triethylamine was dried over KOH pellets before use. Dry THF and toluene were dried by a Pure Solv MD-6 solvent purification system; all other solvents used were reagent grade and used without further purification. Both Heck coupling reactions were performed under an atmosphere of nitrogen. Ozone was produced by an Envirozone Ozonator model VT-5.

1,8-Dibromo-9H-carbazole (1b). To a solution of 1,8-dibromo-3,6-di-tert-butyl-9H-carbazole (1.1254 g, 2.574 mmol) in dry toluene (50 mL) was added anhydrous AlCl₃ (0.9928 g, 7.446 mmol) in small portions. The flask was capped and the orange solution was stirred at RT. After 1 h, the solution had changed to a dark green-brown color. After stirring for 4 h, the reaction was quenched and washed with water $(2 \times 50 \text{ mL})$ and the aqueous phase was further extracted into DCM (3 \times 50 mL). The organic fractions were dried over MgSO₄, filtered, and the solvent was removed under reduced pressure, yielding a pale orange, oily solid. The crude material was dissolved in Et₂O (3 mL) and precipitated by refrigeration (4 °C), resulting in an off-white solid (0.5824 g, 70%) that was filtered and dried under vacuum. ESI(-) MS $(m/z) = 321.8895 [C_{12}H_6NBr_2]^-$. Anal. Calcd for $C_{12}H_7NBr_2$: C, 44.35; H, 2.17; N, 4.31. Found: C, 44.62; H, 2.08; N, 4.11%. ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.320 (NH, s, 1H), 7.963 (4CzH, d[J = 7.6], 2H), 7.601 (CzH, dd[J = 1.2,8.0], 2H), 7.145 (CzH, t [J = 8.0], 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 137.84 (Cz), 128.85 (Cz), 124.94 (Cz), 121.33 (Cz), 119.95 (Cz), 104.56 (Cz). IR (KBr): $(cm^{-1}) = 3454$ (w), 1603 (w), 1559 (w), 1494 (m), 1424 (s), 1298 (s), 1228 (m), 1183 (s), 1144 (w), 890 (w), 830 (w), 757 (s), 724 (s), 678 (w), 568 (w).

1,8-Bis((E)-styryl)-3,6-di-*tert*-butyl-9*H*-carbazole (2a). 1,8-Dibromo-3,6-di-*tert*-butyl-9*H*-carbazole (0.9997 g, 2.287 mmol), styrene (609.1 mg, 5.849 mmol), PdCl₂(PPh₃)₂ (40.8 mg, 0.058 mmol), triethylamine (5 mL), and dry THF (5 mL) were added to a 25 mL heavy-walled reaction chamber, degassed with N2 and tightly closed. The mixture was heated to 115 °C for 24 h (Caution! Pressure). After cooling, water (20 mL) was added and the reaction mixture was extracted with DCM (3×20 mL). The solvent was removed under reduced pressure. The resulting solid was taken up in DCM (ca. 2 mL) and run through a pad of silica (20 mL) using DCM. The solvent was removed under reduced pressure and the resulting crude product was washed with cold cyclohexane, yielding a bright-yellow solid (0.785 g, 71%). ESI(+) MS (m/z) = 506.2827 $[C_{36}H_{37}NNa]^+$. Anal. Calcd for C36H37N·0.5H2O: C, 87.76; H, 7.77; N, 2.84. Found: C, 87.40; H, 7.52; N, 2.81%. ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.296 (NH, s, 1H), 8.043 (4CzH, d [J = 1.5], 2H), 7.659 (CzH, d [J = 1.5], 2H), 7.637 (o-StyH, d [J = 7.6], 4H), 7.488 (Cz-CH=CH, d [J = 16], 2H), 7.424 (m-StyH, t [J = 7.6], 4H), 7.314 (p-StyH, t [J = 7.2], 2H), 7.284 (Cz-CH=CH, d [J = 16], 2H), 1.508 (tBu, s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 143.25 (Cz), 137.67 (Cz-CH=CH-C), 136.41 (Cz), 128.95 (m-Sty), 130.08 (Cz-CH=C), 127.91 (p-Sty), 126.68 (o-Sty), 125.41 (Cz-CH=C), 124.50 (Cz), 121.79 (Cz), 120.59 (Cz), 116.32 (Cz), 34.95 (tBu), 32.21 (tBu). IR (KBr): (cm⁻¹) = 3482 (w), 3028 (w), 2951 (s), 2928 (w), 2865 (m), 1599 (m), 1487 (s), 1393 (w), 1361 (m), 1356 (w), 1280 (m), 1244 (m), 951 (s), 868 (m), 758 (m), 737 (s), 691 (s), 639 (w), 553 (w).

1,8-Bis((E)-styryl)-9H-carbazole (2b). 1,8-Dibromo-9H-carbazole (336.7 mg, 1.036 mmol), $PdCl_2(PPh_3)_2$ (15.3 mg, 0.019 mmol), styrene (328.0 mg, 3.149 mmol), triethylamine (5 mL), and dry THF (5 mL) were added to a 25 mL heavy-walled reaction chamber, degassed with N2 and tightly closed. The reaction chamber was heated at 115 °C for 28 h (Caution! Pressure). After cooling, water (30 mL) was added and the reaction mixture was extracted with DCM (2 \times 25 mL). The combined organic phase was dried over magnesium sulfate and filtered. The solvent was removed under reduced pressure and the resulting powder was loaded onto a column loaded with silica (30 mL) in DCM which was eluted, which yielded a bright-yellow solid (306.8 mg, 80%). ESI(-) MS (m/z) = 370.1604 [C₂₈H₂₀N]⁻. Anal. Calcd for C₂₈H₂₁N: C, 90.53; H, 5.70; N, 3.77. Found: C, 90.40; H, 5.63; N, 3.89%. ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.459 (NH, s, 1H), 8.020 (CzH, d [J = 7.6], 2H), 7.637 (CzH, dd [J = 7.6, 0.8], 2H), 7.630 (o-StyH, dd [J = 8.0, 1.4], 4H), 7.489 (Cz-CH=CH, d [J = 16], 2H), 7.427 (m-StyH, t [J = 7.6], 4H), 7.323 (p-StyH, tt [J = 7.2, 1.2], 2H), 7.296 (Cz-CH=CH, d [J = 16], 2H), 7.295 (CzH, t [J = 7.6], 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 137.72 (Cz), 137.50 (Cz-CH=CH-C), 130.69 (Cz-CH= CH), 128.98 (m-Sty), 128.08 (p-Sty), 126.75 (o-Sty), 124.41 (Cz), 124.39 (Cz-CH=CH), 123.78 (2/7-Cz), 121.40 (1/8-Cz), 120.42 (3/ 6-Cz), 119.97 (4/5-Cz). IR (ATR diam.): (cm⁻¹) = 3464 (w), 3025 (w), 1594 (w), 1491 (m), 1448 (w), 1426 (m), 1420 (m), 1337 (m), 1312 (m), 1221 (m), 1168 (w), 1061 (w), 957 (m), 950 (m), 771 (s), 753 (w), 733 (s), 689 (s), 585 (w), 564 (w), 549 (w), 476 (w).

1,8-Diformyl-3,6-di-tert-butyl-9H-carbazole (3a). Behind a blast shield, a light yellow solution of 1,8-bis((E)-styryl)-3,6-di-tertbutyl-9H-carbazole (307.2 mg, 0.635 mmol) in DCM (50 mL) was cooled to -78 °C (dry ice/acetone) and then subjected to O_3/O_2 (Caution! Highly reactive, potentially explosive ozonides being formed) gas until O_3 saturation in the DCM (<5 min). The resulting greenish solution was purged with nitrogen, resulting in a yellow solution to which DMS (0.5 mL) was added, resulting in a darker yellow solution. The solution was allowed to return to RT and the solvent was removed under reduced pressure, yielding a dark orange solid. The crude material was purified by column chromatography through silica (50 mL) in DCM, yielding a light-yellow solid (R_f 0.48, 146.5 mg, 69%). Anal. Calcd for C₂₂H₂₅NO₂: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.87; H, 7.70; N, 4.13%. ESI(+) MS (m/z) =358.1746 $[C_{22}H_{25}NO_2Na]^+$. ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 11.450 (NH, s, 1H), 10.235 (CHO, s, 2H), 8.405 (CzH, d [J = 2.0], 2H), 7.940 (CzH, d [J = 2.0], 2H), 1.515 (tBu, s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 193.09 (CHO), 143.30 (Cz), 137.12 (Cz), 129.61 (Cz), 123.64 (Cz), 123.58 (Cz), 120.12 (Cz), 34.98 (tBu), 32.05 (tBu). IR (ATR diam.): $(cm^{-1}) = 3429$ (m), 2954 (m), 2899 (w), 2866 (w), 2792 (w), 1671 (m), 1617 (w), 1590 (m), 1481

(m), 1467 (m), 1443 (w), 1395 (w), 1366 (w), 1316 (w), 1267 (w), 1237 (w), 1215 (m), 1204 (w), 1177 (w), 1138 (w), 1110 (w), 1099 (w), 1053 (m), 1023 (w), 946 (w), 914 (w), 879 (m), 816 (w), 781 (w), 754 (w), 728 (w), 710 (w), 669 (w), 639 (s), 623 (s), 567 (w).

1,8-Diformyl-9H-carbazole (3b). Behind a blast shield, a light yellow solution of 1,8-bis((E)-styryl)-9H-carbazole (103.2 mg, 0.462 mmol) in DCM (35 mL) was cooled to -78 °C (dry ice/acetone) and then subjected to O_3/O_2 (*Caution!* Highly reactive, potentially explosive ozonides being formed) gas until O3 saturation in the DCM (<5 min). The resulting greenish solution was purged with nitrogen, resulting in a yellow solution to which DMS (ca. 0.5 mL) was added, resulting in a darker yellow solution. The solution was allowed to return to RT and the solvent was removed under reduced pressure, yielding a dark orange solid. The crude material was purified by column chromatography through silica (30 mL) in DCM, yielding the desired product as a yellow-orange solid (R_f 0.21, 58.3 mg, 95%). Anal. Calcd for C14H9NO2: C, 75.33; H, 4.06; N, 6.27. Found: C, 75.06; H, 4.05; N, 6.00%. ESI(+) MS $(m/z) = 246.0527 [C_{14}H_{9}]$ NO_2Na]⁺. ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 11.724 (NH, s, 1H), 10.253 (CHO, s, 2H), 8.365 (Cz, dt [J = 8.0, 0.8], 2H), 7.918 (Cz, dd [J = 7.2, 1.2], 2H), 7.451 (Cz, t [J = 7.6], 2H). ¹³C NMR (100 MHz, $CDCl_3$) δ (ppm) = 192.82 (CHO), 138.48 (Cz), 132.10 (Cz), 126.98 (Cz), 123.55 (Cz), 120.61 (Cz), 120.16 (Cz). IR (KBr): $(cm^{-1}) = 3432$ (m), 2811 (w), 2737 (w), 1675 (s), 1611 (w), 1591 (s), 1494 (m), 1440 (w), 1385 (m), 1326 (m), 1305 (w), 1222 (m), 1189 (m), 1114 (s), 1066 (w), 1028 (m), 810 (m), 782 (s), 775 (m), 715 (w), 633 (s).

H₂L^{rBu} (**4a**). To a pale yellow refluxing solution of 1,8-diformyl-3,6di-*tert*-butyl-9*H*-carbazole 3a (40 mg, 0.119 mmol) in ethanol (10 mL) was added ethylene diamine (7.2 mg, 0.120 mmol) as an ethanol solution (1 mL). The resulting yellow solution was refluxed for 4 h, initial precipitation appearing after 1 h. After cooling to room temperature, the precipitate was isolated by filtration and washed with ethanol (20 mL) to give the product as a pale yellow solid (38 mg, 88%). ESI (+) MS (*m*/*z*) = 741.4675 [C₄₈H₅₈N₆Na]⁺. Anal. Calcd For C₄₈H₅₈N₆·0.5EtOH: C, 79.31; H, 8.29; N, 11.33. Found: C, 79.19; H, 8.38; N, 11.31. ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 12.079 (NH (5), s, 1H), 8.570 (CH=N (3), s, 2H), 7.818 (CzH (1/2), s, 2H), 6.962 (CzH (1/2), s, 2H), 4.524 (CH₂ (4), s, 4H), 1.285 (tBu (6), s, 18H). UV-vis, (DMF): λ_{max/nm} (ε/dm³ mol⁻¹ cm⁻¹) = 300(14830), 332(17454), 368(11297).

H₂**L**^H (4b). To a pale yellow refluxing solution of 1,8-diformyl-9*H*-carbazole **3b** (50 mg, 0.224 mmol) in ethanol (20 mL) was added ethylene diamine (13.4 mg, 0.230 mmol) as an ethanol solution (1 mL). The resulting yellow solution was refluxed for 4 h, initial precipitation appearing after 1 h. After cooling to room temperature, the precipitate was isolated by filtration and washed with ethanol (20 mL) to give the product as a pale yellow solid (48 mg, 87%). ESI (+) MS (*m*/*z*) = 495.2304 [C₃₂H₂₇N₆]⁺, 517.2119 [C₃₂H₂₆N₆Na]⁺. Anal. Calcd For C₃₂H₂₆N₆·0.2EtOH: C, 77.24; H, 5.44; N, 16.68. Found: C, 77.19; H, 5.45; N, 16.49. ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 13.343 (NH (5), s, 1H), 8.678 (CH=N (3), s, 2H), 8.189 (CzH (1/2), d [*J* = 8.0], 2H), 7.570 (CzH (1/2), d [*J* = 7.2], 2H), 7.300 (CzH (6), t [*J* = 7.2], 2H), 4.284 (CH₂ (4), s, 4H). UV–vis, (DMF): λ_{max/nm} (ε/dm³ mol⁻¹ cm⁻¹) = 285(18313), 315(22854), 355(8768), 369(11071).

[Zn₂L^H(OAc)₂]·CHCl₃ (5b). To a refluxing solution of H₂L^H (110 mg, 0.222 mmol) in CHCl₃ was added a methanol solution (60 mL) of zinc(II) acetate dihydrate (110 mg, 0.501 mmol). To the resulting pale yellow solution was added triethylamine (45 mg, 0.445 mmol), giving a bright yellow solution that was refluxed for 16 h. After cooling, the solvent was removed to give a bright yellow solid which was washed with methanol (100 mL) to give the product as a bright yellow solid (135 mg, 83%). Anal. Calcd For Zn₂L^H(OAc)₂·0.4CHCl₃: C, 55.66; H, 3.90; N, 10.70. Found: C, 55.56; H, 4.04; N, 10.54. ESI (+) MS (*m/z*) = 655.0750 [C₃₂H₂₄N₆Zn₂Cl]⁺. ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.563 (CH=N, s, 2H), 8.328 (CzH, d [*J* = 6], 2H), 7.562 (CzH, d [*J* = 8], 2H), 3.987 (CH_{2b}, d [*J* = 8], 2H). UV–vis, (DMF): λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹) = 309(20925), 335(22253), 368(19092), 412(19450).

Inorganic Chemistry

Single crystals of $[{\rm Zn}_2 L^H(OAc)_2]$ were grown by slow cooling of the reaction solution to room temperature.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02763.

Additional crystallographic data; NMR and fluorescence spectra (PDF) $% \left(PDF\right) =\left(PDF\right) \left(PDF\right) \left(PDF\right) \left(PDF\right) \right) \left(PDF\right) \left(PDF\right$

Accession Codes

CCDC 1542955–1542958 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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