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DOSY NMR, X-ray Structural and Ion-Mobility Mass Spectrometric Studies on Electron-Deficient and Electron-Rich M₆L₄ Coordination Cages

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Supporting Information

ABSTRACT: A novel modular approach to electron-deficient and electronrich M_6L_4 cages is presented. From the same starting compound, via a minor modulation of the synthesis route, two C_3 -symmetric ligands L1 and L2 with different electronic properties are obtained in good yield. The trifluorotriethynylbenzene-based ligand L1 is more electron-deficient than the wellknown 2,4,6-tri(4-pyridyl)-1,3,5-triazine, while the trimethoxy-triethynylbenzene-based ligand L2 is more electron-rich than the corresponding benzene analogue. Complexation of the ligands with cis-protected square-planar $[(dppp)Pt(OTf)_2]$ or $[(dppp)Pd(OTf)_2]$ corner-complexes yields two electron-deficient (1a and 1b) and two electron-rich (2a and 2b) M_6L_4 cages. The single crystal X-ray diffraction study of 1a and 2a confirms the expected octahedral shape with a ca. 2000 Å³ cavity and ca. 11 Å wide apertures. The crystallographically determined diameters of 1a and 2a are 3.7



and 3.6 nm, respectively. The hydrodynamic diameters obtained from the DOSY NMR in $CDCl_3:CD_3OD$ (4:1), and diameters calculated from collision cross sections (CCS) acquired by ion-mobility mass spectrometry (IM-MS) were for all four cages similar. In solution, the cage structures have diameters between 3.3 to 3.6 nm, while in the gas phase the corresponding diameters varied between 3.4 to 3.6 nm. In addition to the structural information the relative stabilities of the Pt_6L_4 and Pd_6L_4 cages were studied in the gas phase by collision-induced dissociation (CID) experiments, and the photophysical properties of the ligands L1 and L2 and cages 1a, 1b, 2a, and 2b were studied by UV–vis and fluorescence spectroscopy.

INTRODUCTION

Over the last 20 years, coordination-driven self-assembly has been demonstrated to be a highly efficient method to produce three-dimensional supramolecular architectures. Rational design of such discrete structures is based on structurally predesigned building blocks, viz. ligands and the known coordination geometries of specific metal cations. Consequently the coordination geometries of the metal ions (M^{n+}) and the number of the binding sites of ligands (L) and overall structure of the ligand define the geometry of the assembly.¹

The simplest of "platonic solid" coordination cages are tetrahedron, cube, and octahedron.¹ Also "higher order" coordination polyhedra are known.² Tetrahedral coordination cages can be prepared by edge-directed self-assembly of C_2 -symmetric bis-bidentate ligands or their subcomponents with suitable, usually octahedrally coordinated metal cations, leading to the M₄L₆ complex.^{1c,d,3} An alternative route, face-directed self-assembly, uses C_3 -symmetric tris-bidentate ligands which upon metal coordination lead to M₄L₄ tetrahedra.^{1e,4} The cubic coordination cages can also be obtained by edge or face-directed self-assembly of bis-monodentate,⁵ bis-bidentate,⁶

tetrakis-monodentate, 7 or tetrakis-bidentate 8 ligands with suitable metal cations.

The pioneering work by Fujita⁹ and Stang¹⁰ has provided the basis for the M_6L_4 cages. Fujita's molecular paneling approach defines trigonal C_3 -symmetric tris-monodentate N-donor ligands as "paneling ligands", which upon complexation with a proper metal cation, leads to M_6L_4 , whereas Stang's approach uses "directional bonding", which under similar conditions leads to analogous M_6L_4 cages. The generally used metal cations are the cis-protected square-planar Pd(II) and Pt(II) "corner"-complexes with two labile anionic ligands (typically nitrates or triflates) at 90° angle available for N-ligand binding. The Fujita's approach uses mostly ethylenediamine as a protective group for the metal, whereas Stang's approach uses the more robust bisphosphino complex.¹¹ The directional bonding approach (Stang) defines the M_6L_4 cage as a truncated tetrahedron, where the ligands act as the faces of a tetrahedron, while the ditopic metals are placed in the middle of the edges,

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whereas the molecular paneling approach (Fujita) refers to $M_{\rm o}L_4$ as an octahedron with the paneling ligands as the faces and the metal ions as the vertices.

Until now, eight trigonal C_3 -symmetric tris-monodentate Ndonor ligands with either pyridine or cyano groups as the donors have been used in the construction of M_6L_4 cages (Figure 1).^{9,10,12} Additionally, there are other ligands, mostly



Figure 1. Similar ligands (A-H) previously used in M₆L₄ cages.^{9,10,12}

nonplanar, used in M6L4 cages as well.¹³ A common modification of the well-known electron-deficient triazine ligand (Figure 1, A)⁹ toward larger-sized M₆L₄ cages has been the addition of aromatic ring(s) between the central triazine ring and the donor groups (Figure 1, B-D).9,12a A benzene core has been used together with ethynyl or ethenyl moieties (Figure 1, E and G).^{10,12b,c} Cyano groups as *N*-donors have been used instead of pyridine in smaller (Figure 1, \mathbf{F})^{12d} or larger (Figure 1, \mathbf{H})^{12b} versions. Also, changing the protecting groups around the metal cation^{10,12b,c,14} or the metal itself^{12d,13c,15} has been another way of modifying the cages. Surprisingly the modification of the central benzene core (Figure 1, E)^{10,12b,c} has not been explored. Herein we report the synthesis and characterization of two new C3-symmetric ligands L1 and L2, their self-assembly with Stang's Pt or Pdcorner-complexes,¹¹ [(dppp)Pt(OTf)₂] and [(dppp)Pd- $(OTf)_2$] (dppp = 1,3-[bis(diphenylphosphino)]-propane), into M₆L₄ cages 1a, 1b, 2a, and 2b and their full characterization by NMR spectroscopy, single-crystal X-ray diffraction, mass spectrometry, ion-mobility mass spectrometry, UV-vis and fluorescence spectroscopy. To the best of our knowledge, this is the first time the size of coordination cages has been studied in three different states of matter as thoroughly, including also information by techniques such as DOSY NMR and IM-MS. The concerted use of three complementary structural techniques allows for the comparison of the sizes of the coordination cages in solution, solid state, and gas phase.

RESULTS AND DISCUSSION

Ligand Design and Self-Assembly of M_6L_4 Cages. Inspired by Stang et al.'s^{10,12b,c} work on M_6L_4 coordination cages and the possibility to tune the properties of the central benzene ring, two C_3 -symmetric target ligands, either electrondeficient with a trifluoro-triethynylbenzene core or electronrich with a trimethoxy-triethynylbenzene core, were prepared starting from commercially available 1,3,5-trifluoro-2,4,6triiodobenzene (Scheme 1) by adapting a known procedure.¹⁶ The ligand L1, 1,3,5-tris[(4-pyridyl)ethynyl]-2,4,6-trifluoroben-

Scheme 1. Syntheses of Ligands and Self-Assembly of M_6L_4 Cages 1a, 1b, 2a, and $2b^a$



^aReaction conditions for ligand L1: (i) 4-ethynylpyridine, [Pd-(PPh₃)₂Cl₂], CuI, *i*-Pr₂NH, 70 °C, 48 h, 41% and for ligand L2: (ii) (a) NaOCH₃, 1,3-dimethyl-2-imidazolidinone, r.t., 18 h, 69%, (b) same conditions as in (i) 59%. (iii) L1 or L2 (4 equiv), [(dppp)M(OTf)₂] (M = Pt, Pd; 6 equiv), CHCl₃:CH₃OH (4:1), 60 °C, 2 h.

zene, was prepared via Sonogashira coupling with 4ethynylpyridine, while the ligand L2, 1,3,5-tris[(4-pyridyl)ethynyl]-2,4,6-trimethoxybenzene, was synthesized by nucleophilic aromatic substitution followed by Sonogashira coupling (Scheme 1). The ethynyl spacers between the pyridine rings and the trifluoro- or trimethoxybenzene core make the ligands L1 and L2 and the resulting M_6L_4 cages larger than the corresponding M_6L_4 cages containing the ligand A, and at the same time allowing the ligand to adopt planar conformation needed for the successful cage formation. A small change in the synthesis protocol (Scheme 1) from the same starting material (1,3,5-trifluoro-2,4,6-triiodo-benzene) results in a modulation of the electron density of the benzene core. The trifluoro ligand L1 is strongly electron-deficient, while the trimethoxy analogue L2 is electron-rich. Using these ligands with cis-protected Stang's corner-complex¹¹ $[(dppp)M(OTf)_2]$ (M = Pd or Pt) leads to four new large M_6L_4 octahedral cages 1a, 1b, 2a, and **2b** (Scheme 1).

The electrostatic potential surfaces were calculated¹⁷ for ligands L1, L2, triazine ligand A, and tris-ethynylbenzene ligand E (Figure 2). The strongly electron-withdrawing fluorine atoms at 2-, 4- and 6-positions, in addition to electron-withdrawing ethynyl moieties at 1-, 3-, and 5-positions, substantially decrease the electron density of the benzene core of ligand L1 making it more electron-deficient than the triazine ligand A (Figure 2).

The trimethoxy ligand L2, on the other hand, has more electron-rich benzene core compared to the ligand E (Figure 2), due to the electron donating effect of methoxy groups (Figure 2). In addition to the molecular M_6L_4 cages, Fujita et al. have utilized the electron-deficiency of triazine ligand A in trapping electron-rich guests inside 3D coordination networks¹⁸ and pillared coordination cages.¹⁹

The complexation of Pt- or Pd-corner complex (6 equiv) with ligand L1 or L2 (4 equiv) in $CHCl_3:CH_3OH$ (4:1) at 60 °C for 2 h, followed by precipitation with hexane, afforded



Figure 2. Electrostatic potential surfaces of A, E, L1, and L2. The structures are optimized at the B3LYP level of theory using the $6-31G^*$ basis set in vacuum.¹⁷ Red and blue represent negative and positive charge densities, respectively.

white solids 1a-b and 2a-b (Scheme 1). The ¹H NMR analysis shows one set of ligand proton signals indicating a highly symmetrical assembly (Figure 3a). The PyH_{α} signals of fluorine substituted cages are shifted downfield by ($\Delta\delta$) 0.36 (1a) and 0.30 ppm (1b), whereas the PyH_{β} signals move upfield by $(\Delta\delta)$ –0.31 (1a) and –0.35 (1b) ppm as a result of the metal-ligand complexation. Only one band is observed in the ¹H DOSY NMR spectra for fluorine cages 1a and 1b with diffusion coefficients (D) of $2.35 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ (1a, Figure 3b) and $2.29 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (1b, Figure 3c), which correspond to spherical hydrodynamic diameters of 3.5 (1a) and 3.6 nm (1b). Similarly, for the methoxy substituted cages, 2a and 2b, complexation was confirmed by ¹H NMR (Figures S4, S16, and S21). Also, the hydrodynamic diameters obtained by ¹H DOSY NMR were similar in size, viz. 3.3 nm (2a) and 3.6 nm (2b) with the corresponding fluorine-containing cages (Figures S20 and S25). The hydrodynamic diameters are fully consistent with crystal structures of 1a and 2a as well as with the diameters calculated from collision cross sections (CCS) obtained from the ion-mobility mass spectrometry (IM-MS) experiments (see below, Table 1). The ³¹P NMR (Figures S9, S14, S19, and S24)

and ¹⁹F NMR spectra (Figures S8 and S13) also support the formation of a single, highly symmetrical product.

Crystallography. Despite the 20-year history of M_6L_4 cages, surprisingly few good quality crystal structures have been published. Several crystal structures of complexes with the triazine ligand A were reported by Fujita et al. in 2002.²⁰ The electron-deficient Pd_6L_4 (L = the triazine A) cage with the cavity volume of ca. 750 Å³ exhibits rich host-guest chemistry due to the suitably sized cavity for complete encapsulation of one, two, or four electron-rich guest molecules, depending on the size of the guest, viz. one tetrabenzylsilane (molecular volume = $MV = 458 \text{ Å}^3$) or tri-*tert*-butylbenzene (MV = 320Å³), two diphenylmethane (MV = 202 Å³) or 1,2-bis(4methoxyphenyl)-1,2-ethanedione (MV = 279 Å³) or four ocarborane (MV = 172 Å³) or 1-adamantanol molecules (MV = 172 Å³). A smaller version of the M_6L_4 cage with the cavity volume of ca. 500 Å³ using tricyanobenzene (Figure 1, ligand F) as the ligand has been reported by Lusby et al.^{12d} Their cage encapsulates four triflate anions (MV = 86 $Å^3$) symmetrically arranged around the center of the cavity. The largest M_6L_4 cage with 1,3,5-tris(4-pyridylethynyl)benzene (Figure 1, ligand E) and 1,3,5-tris(4-pyridyl-trans-ethenyl)benzene (Figure 1, ligand G) as the ligands has been reported by Stang et al. $^{\rm 12c}$ Because of the very large size of the cavity, large apertures (windows), and moderate crystal quality, no solid state host-guest complexation was observed. The overall size of the cavities of M_6L_4 cages made by Stang et al. is comparable to the cages 1a and 2a reported in this work; only the windows are smaller in 1a and 2a (see below).

Since only weak diffraction was observed with crystals of 1a and 2a (Figure 4), obtained by slow diffusion of hexane (1a) or acetone (2a) into a CHCl₃:CH₃OH (4:1) solution, the data collections were done using synchrotron radiation (see Supporting Information). In spite of numerous attempts with several different crystallization conditions, the corresponding Pd_6L_4 cages 1b and 2b did not form single crystals, and only powdery precipitate was obtained.

The Pt_6L_4 complexes **1a** and **2a** are discrete self-assembled supramolecular cages with an octahedral overall structure. The four pseudotrigonal ligands (**L1** or **L2**) form a large octahedrally shaped cavity with a radius of 8 Å (measured from the center of the cavity to the centroids of the central benzene ring of the paneling ligand) and volume of ca. 2000 Å³.



Figure 3. (a) Partial ¹H NMR (300 MHz, CD₂Cl₂, 303 K) spectra of ligand L1, cages 1a and 1b (top to bottom). Partial ¹H DOSY NMR (400 MHz, CDcl₃:CD₃OD 4:1, 298 K) spectra of cages (b) 1a and (c) 1b.

Table 1. CCS _{exp}	Values of $[M_6L_4(OTf)_8]^{4+}$	Ions and Comparison of Diameter	rs Obtained by IM-MS,	¹ H DOSY NMR and X-ray
Diffraction				

cage	m/z^a	ion	CCS_{exp} $(\text{\AA}^2)^b$	IM-MS $d (nm)^c$	DOSY $d (nm)^d$	X-ray $d (nm)^e$
1a	1645	$[Pt_6L1_4(OTf)_8]^{4+}$	926 (mi)	3.4	3.5	3.7
			945 (ma)	3.5		
1b	1512	$[Pd_6L1_4(OTf)_8]^{4+}$	962 (mi)	3.5	3.6	
			982 (ma)	3.5		
2a	1681	$[Pt_6L2_4(OTf)_8]^{4+}$	965 (ma)	3.5	3.3	3.6
			988 (mi)	3.5		
2b	1548	$[Pd_6L2_4(OTf)_8]^{4+}$	989 (ma)	3.6	3.6	
			974 (mi)	3.5		

^{*a*}Most abundant m/z. ^{*b*}ma = major conformer, mi = minor conformer in ion mobilogram. ^{*c*}Calculated on the basis of CCS by assuming a spherical shape of the metal cage. ^{*d*}Calculated using Stokes–Einstein equation. ^{*e*}The average of the distance of the opposite H atoms +1.2 Å.



Figure 4. Crystal structures of 1a (top) and 2a (below), ball-and-stick (left), and space-filling models (right).

The cages have four large similar trigonal apertures, "windows", with a diameter of ca. 11 Å (Figure S26), the size of the windows being slightly smaller in 2a due to the methoxy substituents. Nine out of the 12 methoxy substituents in the central benzene rings point toward the interior of the cavity 2a, two pointing outside and one parallel with the benzene ring.

The X-ray structure of the uncomplexed ligand L1 (Figures S27-S28) reveals the ligand itself to have a pseudotrigonal structure, showing marked deviations from the optimal 120° angles. The angles between the central benzene ring and the pyridine rings (Bz-Py, Figure S29) vary from 105.1 to 131.1°. This is also reflected in the N…N distances which vary from 13.09 to 15.00 Å (Figure S30), whereas the calculated structure of L1 (obtained using SPARTAN¹⁷) shows N···N distances of 14.30 Å with a perfect trigonal symmetry. In addition to the deviation from the trigonal angles, also small deviations from planarity are observed (Figure S31), with the twist angle between the pyridine ring and the central 2,4,6-trifluorobenzene ring varying from -0.6 to $+14.75^{\circ}$, the planarity being enhanced by quite strong $\pi - \pi$ interactions observed in the crystal lattice of L1. Upon complexation with the Pt- or Pdcorner complexes the ligands L1 and L2 adopt a more trigonal

structure resulting in a coordination cage, which only slightly deviates from a regular octahedron. The four ligands and the four windows have all nearly the same dimensions, viz. ca. 14.5 Å, with N…N distances within the ligand varying from 13.73 to 14.64 Å for 1a and 13.73 to 14.77 Å for 2a. The trigonal angles in the cages 1a and 2a approach the ideal values, now being $111.7-127.6^{\circ}$ for 1a and $115.1-128.2^{\circ}$ for 2a. The lack of short contacts in the crystal structures of cages 1a and 2a allows a small twisting of the pyridine rings with respect to the central benzene ring, the twist angles varying from -12.3° to 5.13° for 1a and -13.5° to 11.00° for 2a.

Mass Spectrometry. The electrospray ionization mass spectra (ESI-MS) measured from 50 μ M solutions of 1a, 1b, 2a, and 2b in CH₂Cl₂ show discrete peaks corresponding to ions $[M_6L_4(\text{OTf})_{12,n}]^{n+}$ (n = 3-5) (Figures 5a, S32, S33).



Figure 5. (a) ESI-TOF MS spectrum of **1a** (50 μ M in CH₂Cl₂). Inset shows the fit of theoretical isotopic distribution (red solid line) (b) ion mobilogram (green line) for ion m/z 1644 corresponding to $[(dppp)Pt_6(L1)_4(OTf)_8]^{4+}$.

Intact M_6L_4 cages were observed as major products in each spectrum, although minor peaks for M_5L_4 , M_4L_4 , and M_4L_3 were evident, especially in samples of more labile Pd-cages. These smaller ions do not necessarily originate from fragmentation, but they may result from the instability of cages in μ M-regime concentration used in the ESI-MS experiments, which is a common outcome with coordination complexes.²¹

The drift tube ion-mobility mass spectrometry (IM-MS) experiments confirmed $[M_6L_4(OTf)_{12-n}]^{n+}$ ions to have CCS values consistent with the crystal structures and the hydrodynamic diameters obtained by ¹H DOSY NMR (Table 1). Assuming a spherical shape for M_6L_4 cages, the diameters

obtained from the crystal structures, hydrodynamic diameters (DOSY NMR) and the CCS-derived diameters (IM-MS) were all within 0.1–0.3 nm of each other. The values obtained with different techniques and in different states of matter are similar, indicating that any of these methods will give reliable results when carefully executed.²²

As the drift tube of the IM-MS instrument is operated at atmospheric pressure, it allows high resolution separations and therefore accurate determination of CCS values without the need for cumbersome calibration, which often severely complicates the analysis done by using more common traveling-wave ion mobility MS (TWIM-MS).^{22b} Consequently. the drift tube IM-MS is an ideal method to study gas phase shape and CCS values of metal cages with high resolution. It should be emphasized that IM-MS has not yet been widely applied to study gas-phase conformations of metal-organic cages or metal-organic structures.^{22,23} Therefore, the comparison of CCS values with the DOSY NMR and crystal structures underlines the potential of IM-MS and verifies its applicability to structural studies of metal-organic cages. Especially when characterization through traditional methods (X-ray and NMR spectroscopy) is challenging or impossible, the IM-MS appears to be a highly valuable alternative.

For each $[M_6L_4(OTf)_8]^{4+}$ ion, two conformers were observed in ion mobilograms, one major and one minor (Figure 5b, S39). In most cases, the major conformer constituted ca. 80% of ion population, and the difference in CCS values between the conformers was only ca. \pm 20 Å² (ca. 4–5 Å in diameter). It is, therefore, reasonable to assume that the conformations arise from variation in locations of the two triflate anions which exceed the number of metal centers in $[M_6L_4(OTf)_8]^{4+}$. This is also supported by the mobilogram of $[M_3L_4(OTf)_6]^{4+}$ (Figure S39) which shows only a single conformer (only one triflate exceeding the number of metal corners).

The isolated $[M_6L_4(OTf)_8]^{4+}$ ions were further studied in the gas phase by collision induced dissociation (CID) experiments (Figure 6, S36). In the qualitative sense, all metal cages



Figure 6. CID dissociation curves of isolated ions $[M_6L_4(OTf)_8]^{4+}$ for cages 1a and 1b.

dissociated similarly and produced structurally characteristic fragment ions through eliminations of $[M(OTf)]^+$, $[ML-(OTf)]^+$, and $[M_2L(OTf)_2]^{2+}$. The elimination of two metal corners at most was in every case followed by elimination of a ligand, which is well in line with the cage-like structure. The experiments as a function of increased collisional activation revealed a clear stability difference between cages **1a** and **1b**, the former being more stable (Figure 6). Between cages **2a** and

2b, such a stability difference was not observed (Figure S36). This behavior can be rationalized through stability differences between the metal corners. Because of the electron-with-drawing nature of ligand L1, the properties of metal—nitrogen bonds are more reflected in the overall gas phase stability of the cage. The differences between the two metal centers are also reflected in the experimental CCS values; the Pt-cages showing smaller CCS values (shorter coordinative bonds) compared to the corresponding Pd-cages. In addition, the difference between the CCS values in Pd- and Pt-cages with ligand L1 is evidently larger compared to same difference between cages with L2 (Table 1).

The mixed ligand experiment (both ligands present in equimolar ratio) further confirmed the ability of the both ligands to form a cage with Pt(II), with the formation of all three possible heterometallic cages $[M_6L1_nL2_{4-n}]$ (n = 0-4)observed experimentally (Figure S37). The formation of cages with ligand L2 was only slightly favored over statistical distribution. A similar mixed-metal experiment (both metals present in equimolar ratio with one ligand) showed also closeto-statistical distribution of heterometallic cages (Figure S38), although the abundance of the cages was drastically lower compared to ones formed with only one metal. In the heterometallic experiment there was also increased abundance of the M5L4 fragments. This indicates a decreased stability of heterometallic cages, most probably due to slight distortion of cage. In addition, the observation of close-to-statistical distribution implies kinetic control in the formation of cages.

Photophysics. Distinct differences were observed in the absorption spectra of ligands L1 and L2 (Figure 7a). Electrondeficient L1 showed two sharp absorption bands of similar



Figure 7. (a) Absorption and (b) emission spectra of ligands (4 μ M) and cages (1 μ M) in CH₂Cl₂.

intensity at 284 and 301 nm (Table 2). A relatively broad shoulder was observed around 269 nm with a slightly lower

	λ_{\max} Abs (nm)	molar extinction coefficient $(\varepsilon) \ (\mathrm{cm}^{-1} \ \mathrm{mol}^{-1})$	$\lambda_{\max} \operatorname{Em} (\operatorname{nm})$	quantum yield Φ (%)
L1	269	67600	350	11.5
	284	93700	360	
	301	87900	375	
L2	303	88400	380	45.3
	313	86500		
1a	306	367000	358, 375, 385	8.0
	324	397000		
1b	305	294000	nop ^a	
	322	336000		
2a	341	398000	438	36.3
2b	337	521000	nop ^a	
^a No c	observable	peak.		

Tabl	le 2	. Photop	hysical	Properties	of	Ligands	and	Cages
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intensity. The more electron-rich system L2 showed broader, low-energy, almost equally intense absorption bands at 303 and 313 nm. A starker contrast was observed in the emission spectra of the two ligands (Figure 7b). The observed Stokes shifts were to a similar extent of 70–80 nm for both of the ligands. However, L2 had a typical broad spectra centered around 380 nm, whereas L1 showed a structured emission with three peaks at 350, 360, and 375 nm. This was distinctly different from the modestly broad, unstructured spectra observed for analogous compounds.¹⁶ The quantum yield of L2 was found to be significantly higher than L1 (Table 2), which was in good agreement with reported values for similarly substituted 1,3,5-tris(ethynylphenyl)benzene analogues.¹⁶

The corresponding Pt- and Pd-cages (M_6L_4) for ligands L1 and L2 showed distinctly broader absorption spectra with characteristic red shifts to that of the free ligands (Figure 7a). Both Pt and Pd-cages of L2, 2a, and 2b, showed a broad absorption peak at 341 and 337 nm, respectively, with markedly higher intensity than the free ligands (Table 2). However, the corresponding cages of L1, 1a, and 1b, had similar absorption profiles characterized by two almost equally intense peaks. The 1a showed two absorption bands at 306 and 324 nm, while the corresponding bands appeared at 305 and 322 nm for 1b.

It can be argued that the absorbance spectra of the cages are ligand-centric and are weakly affected by coordinated metals. However, the emission spectra of the cages were critically influenced by the metal. While Pt-cages showed moderate to high emission intensity, especially in case of 2a, Pd coordination drastically quenched any fluorescence from the ligands (Figure 7b). Cage 1a showed a broad spectrum with vibrational structure with peaks at 358, 375, and 385 nm. The emission spectrum of 2a was devoid of any vibrational structure and was centered around 438 nm.

CONCLUSIONS

The modular approach in the design of two new C_3 -symmetric ligand for the construction of M_6L_4 coordination cages is presented. Either electron-withdrawing fluorine or electron-donating methoxy substituents modulate the electronic properties of the ligand, and thus electron-deficient (1a and 1b) and electron-rich (2a and 2b) M_6L_4 cages are obtained. Crystal structures of Pt-cages 1a and 2a expectedly showed them to be

octahedral with a large open cavity punctured by four apertures. The host-guest chemistry studies of the cages will be presented in a future publication. In gas phase, collision cross section-based diameters for all cages were obtained by drift tube ion-mobility mass spectrometry (IM-MS). Moreover, using the collision-induced dissociation (CID) of the parent cage ions, the relative stabilities of the complexes in the gas phase could be established and correlated with the electronic properties of the ligands as well as the nature of the metal centers.

Detailed solution studies by NMR proved the highly symmetrical structure of the M_6L_4 cages and gave the hydrodynamic diameters in very good agreement with the values obtained in solid state and gas phase studies.

The photophysical properties of the ligands and the corresponding cages were shown to be critically dependent on the substituents on the core benzene ring. The ligands, especially electron-rich L2 and the corresponding Pt-cage (2a), were shown to be strongly emissive and could be used in the future to develop capsules that act as fluorosensors upon guest encapsulation.

Our results highlight the importance of the combined structural studies of metallosupramolecular assemblies in the solid state, solution, and gas phase, particularly emphasizing the applicability and reliability of the ion-mobility mass spectrometry (IM-MS) in the structural studies of supramolecular coordination complexes.

ASSOCIATED CONTENT

S Supporting Information

Experimental procedures, synthesis, and characterization data for ligands and M_6L_4 cages, and their MS, IM-MS, and X-ray diffraction data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01082.

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Notes

The authors declare no competing financial interest.

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