Electronic Supplementary Information

Mg−Mg-bonded compounds with *N*,*N*′-dipp-substituted phenanthrene-diamido and *o*-phenylene-diamino ligands

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S1. Experimental details

S1.1 General considerations

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of argon. Solvents were dried by refluxing over and distillation from sodium/benzophenone (hexane, toluene, and THF) or calcium hydride (dichloromethane). Potassium metal and anhydrous $MgCl_2$ were purchased from Alfa Aesar. The starting materials KC_8, $PhCH_2K$,[S1] $PDAH_2$,[S2] *N*,*N*'-dipp-substituted phenanthrene-9,10-diimine,[S3] were prepared by literature procedures.

S1.2 Synthesis of compounds 2 and 3

$[K(THF)_3]_2[L^2Mg{-}MgL^2]$ (2). Potassium (0.027 g, 0.69 mmol) was added to a solution of $\mathbf{L^2}$ (0.12 g, 0.23 mmol) in THF (20 mL) at room temperature. The mixture was stirred for 24h and then anhydrous $MgCl_2$ (0.022 g, 0.23 mmol) was added. After stirring for 48h, the mixture was filtered to give a purple solution. Dark purple crystals were isolated upon slow evaporation of the filtrate. Yield: 0.11 g, 59%. M.p.: 138 ℃ (decomp.) ^{1}H NMR (400 MHz, THF-d_8 , 298 K): δ = 0.64 (d, J = 6.8 Hz, 24H, CH(CH_3)$_2$), 1.05 (d, J = 7.2 Hz, 24H, CH(CH_3)$_2$), 1.69 (THF), 2.27 (toluene), 3.64 (sept, 8H, CH(CH$_3$)$_2$), 3.54 (THF), 6.56 (t, J = 7.6 Hz, 4H, *m*-CH), 6.62 (m, 4H, *m*-CH), 6.74 (m, 4H, *p*-ArH), 6.82 (d, J = 7.6 Hz, 8H, *m*-ArH), 7.09 (toluene), 7.15 (toluene), 7.45 (d, J = 8.0 Hz, 4H, *o*-CH), 8.31 (d, J = 7.6 Hz, 4H, *o*-CH). ^{13}C NMR (100.6 MHz, THF-d_8, 298 K): 24.0, 26.2 (CH(*C*H$_3$)$_2$), 27.9 (*C*H(CH$_3$)$_2$), 122.6, 122.7, 123.8, 126.1 (Ar-C), 126.3, 141.4, 117.6, 118.3, 130.3, 139.0, 155.6 (phenanthrene-C). IR (KBr, ν/cm^{-1}): 3058(w), 2960(vs), 2863(s), 1664(w), 1459(m), 1477(m), 1419(vs), 1357(vs), 1322(vs), 1284(w), 1251(s), 1226(w), 1054(m),1024(m), 883(w), 862(w), 786(m), 752(s), 717(m); elemental analysis calcd (%) for $C_{50}H_{66}KMgN_2O_3$ (806.45): C, 74.46; H, 8.25; N, 3.47. Found: C, 74.96; H, 7.98; N, 3.62.

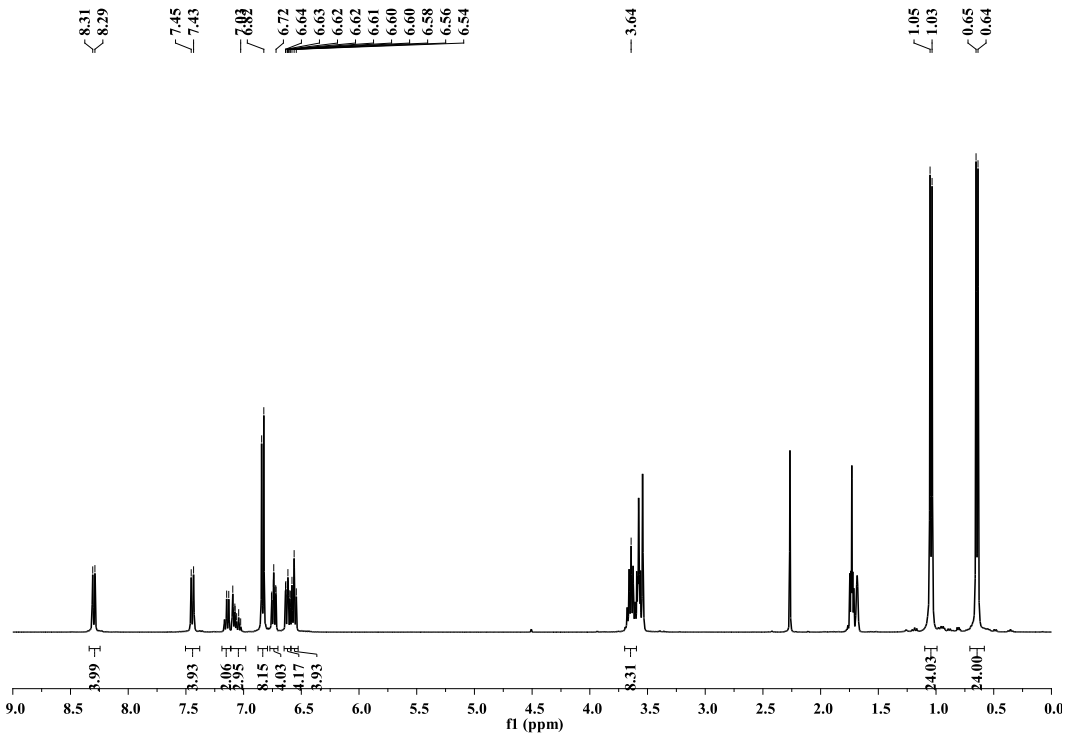


Fig. S1 ^{1}H NMR spectrum of compound **2**.

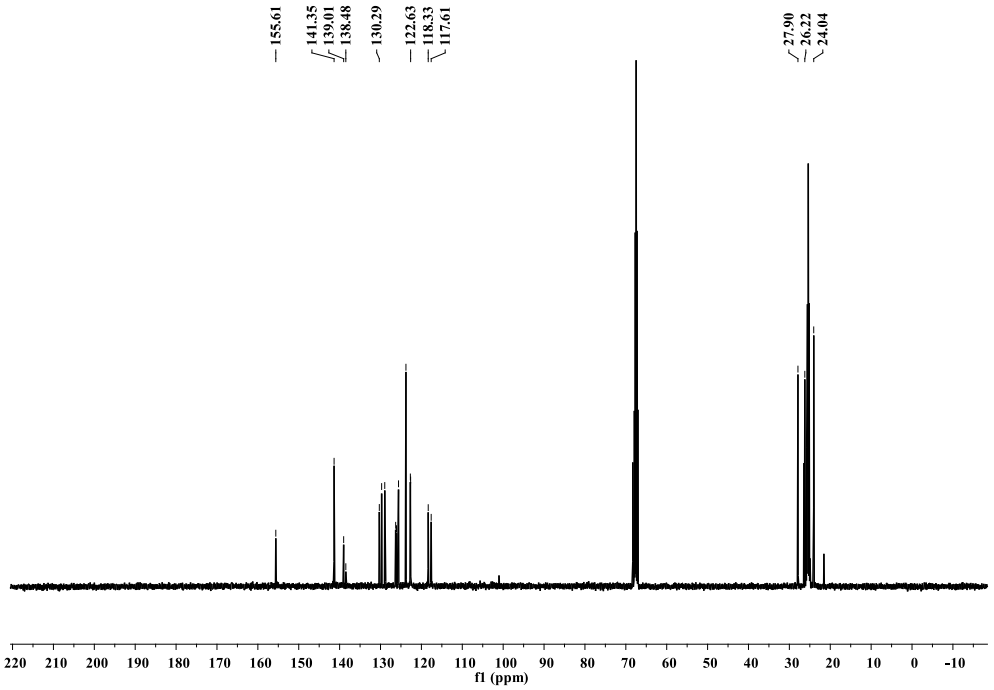


Fig. S2 ^{13}C NMR spectrum of compound **2**.

[K(THF)$_3$]$_2$[L^{3}Mg−MgL^3] toluene (3). To a solution of H_2**L**^{3} (0.34 g, 0.80 mmol) in THF cooled to −40 °C was added benzylpotassium (0.23 g, 1.70 mmol). The mixture was allowed to warm to room temperature and stirred for 20 min. Then anhydrous $MgCl_2$ (0.076 g, 0.80 mmol) was added, and the solution immediately turned green. After 24 h KC_8 (0.12 g, 0.88 mmol) was added and the mixture was stirred for 2 d. It was filtered, the yellow solution concentrated to ca. 4 mL, and 1 mL toluene was added. Leaving the solution at room temperature for a week gave yellow crystals. Yield: 0.34 g, 56%. M.p.: 165 ℃ (decomp.). ^{1}H NMR (400 MHz, THF-d_8, 298 K): δ = 0.80 (d, J = 8.0 Hz, 24H; CH(CH_3)$_2$), 0.90 (d, J = 4.0 Hz, 24H; CH(CH_3)$_2$), 1.72 (THF), 3.11 (m, 8H; CH(CH$_3$)$_2$), 3.57 (THF), 5.33 (m, 4H, *o*-Ar-H), 5.74 (m, 4H; *m*-Ar-H), 6.77 (m, 4H; *p*-Dipp-H), 6.86 (m, 8H; *m*-Dipp-H). ^{13}C NMR (100.6 MHz, THF-d_8, 298 K): 24.9 (CH(*C*H$_3$)$_2$), 26.4 (CH(*C*H$_3$)$_2$), 26.4 (THF), 28.3 (*C*H(CH$_3$)$_2$, 68.3 (THF), 106.2 (*p*-Dipp-C), 110.6 (*m*-Ar-C), 121.5 (*m*-Dipp-C), 122.9 (*o*-Ar-C), 145.6 (*o*-Dipp-C), 150.8 (Dipp-C$_{ipso}$), 151.4 (Ar-C$_{ipso}$). IR: (KBr, ν/cm^{-1}): 3052(w), 2964(s), 2864(s), 1573(w), 1486(m), 1459(s), 1363(m), 1320(m), 1253(m), 1180(m), 1068(s), 908(m), 790(w), 736(w).

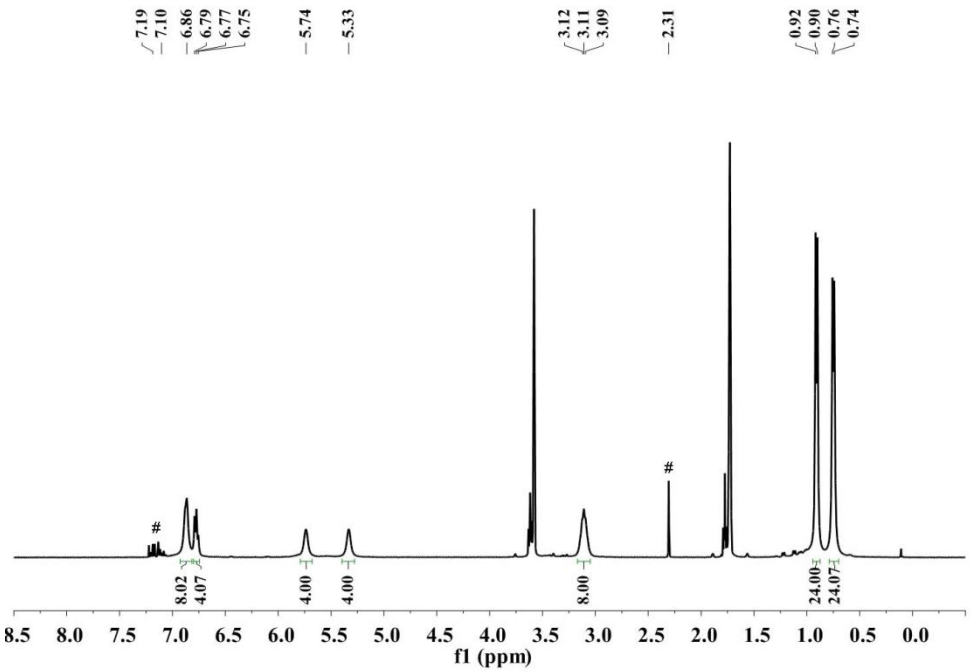


Fig. S3 ^{1}H NMR spectrum of compound **3** ($^{\#}$ marks signals for solvent toluene).

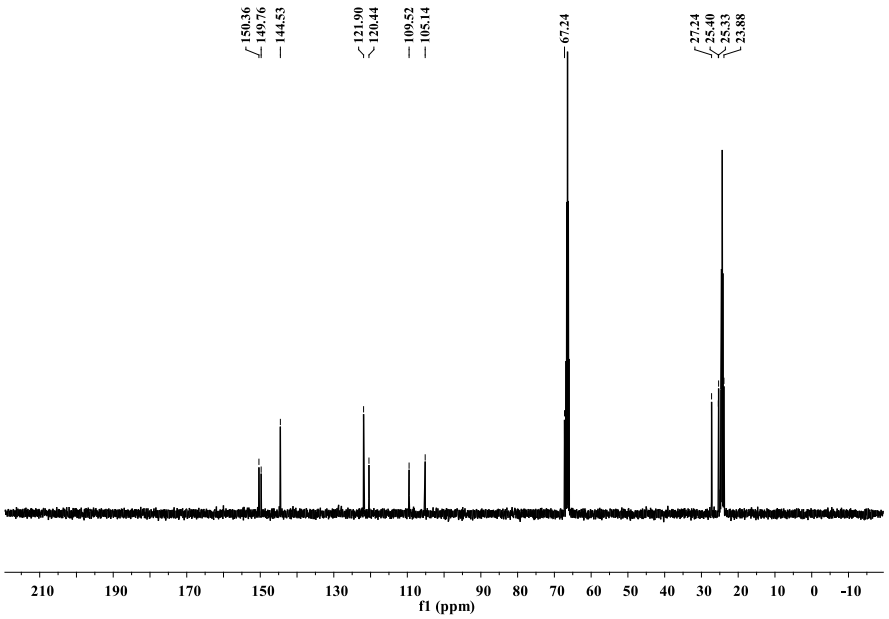
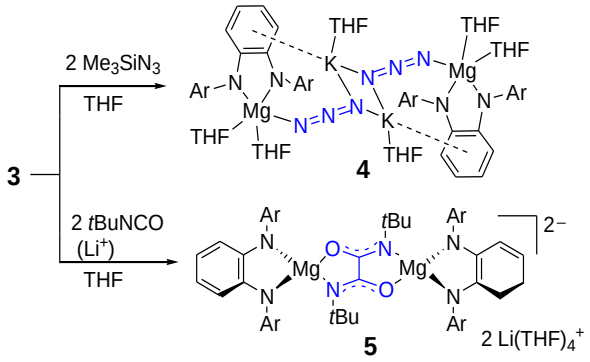


Fig. S4 ^{13}C NMR spectrum of compound **3**.

S1.3 Reactions of compound 3 and characterization of products 4 and 5.



[LMg(THF)$_2$K(THF)(μ-N$_3$)$_2$K(THF)Mg(THF)$_2$L] ·2THF (4). Me_3SiN_3 (33 μL, ca. 29 mg, 0.25 mmol) was added to a cooled (–40 ℃) solution of *in situ* prepared **3** (0.19 g, 0.12 mmol) in THF and the mixture was stirred at room temperature for 2 d. Colorless crystals of product **4** were grown from a concentrated solution at room temperature. Yield: 0.14 g, 70%. M.p.: 150 ℃. ^{1}H NMR (400 MHz, C_6D_6, THF-d_8, 298 K): δ = 1.28 (d, J = 8.0 Hz, 24H, CH(CH_3)$_2$), 1.38 (d, J = 8.0 Hz, 24H, CH(CH_3)$_2$), 3.91 (sept, 8H, CH(CH$_3$)$_2$), 5.84 (m, 4H, *o*-Ar-H), 6.06 (m,2H, *m*-Ar-H), 7.01 (m, 4H, *p*-Dipp-H), 7.26 (m, 8H, *m*-Dipp-H). ^{13}C NMR (100.6 MHz, C_6D_6, THF-d_8, 298 K): 24.5 (CH(*C*H$_3$)$_2$), 26.2 (CH(*C*H$_3$)$_2$), 26.5 (THF), 28.2 (C*H*(CH$_3$)$_2$, 68.1 (THF), 108.4 (*p*-Dipp-C), 111.3 (*m*-Ar-C), 121.9 (*m*-Dipp-C), 123.7 (*o*-Ar-C), 146.4 (*o*-Dipp-C), 151.1 (Dipp-C$_{ipso}$), 153.7 (Ar-C$_{ipso}$). IR (KBr, ν/cm^{-1}): 3050(w), 2960(s), 2865(s), 2150(m, N=N=N), 2100(s, N=N=N), 1575(m), 1538(m), 1457(s), 1380(s), 1359(m), 1317(m), 1259(m), 1180(m), 1101(m), 1049(m), 948(w), 904(w), 788(m), 736(m).

[Li(THF)$_4$]$_2$[(L^{3}Mg)$_2$(*t*BuNCO)$_2$] ·THF (5). *t*BuNCO (29 μL, ca. 25 mg, 0.25 mmol) was added to a cooled (–40 ℃) solution of *in situ* prepared compound **3** (0.12 mmol) in THF, and the mixture was stirred at room temperature for 1 d. Orange crystals of the product **5** were grown from a concentrated solution at room temperature, in which the Li$^+$ counter-cation might come from some Li-containing impurities during the synthesis of PhCH$_2$K from *n*BuLi reagent. The isolated yield of the single crystals is rather low (less than 10%). M.p.: 145 ℃ (decomp.). ^{1}H NMR (400 MHz, THF-d_8, 298 K): δ = 0.92 (b, 48H, CH(CH_3)$_2$), 1.14 (s, 18H, C(CH_3)$_3$), 1.73 (THF), 3.57 (THF + CH(CH$_3$)$_2$), 5.47 (m, 4H, *o*-Ar-H), 5.70 (m, 4H; *m*-Ar-H), 6.67 (m, 4H; *p*-Dipp-H), 6.86 (m, 8H; *m*-Dipp-H). Due to the very poor solubility of the product, ^{13}C NMR could not be obtained. IR (KBr, ν/cm^{-1}): 3045(w), 2960(s), 2865(s), 1577(w, NCO), 1533(s), 1469(s), 1425(s), 1313(s), 1263(s), 1180(m), 1051(s), 900(m), 784(m), 728(m).

Since compound **5** contains the undesired Li$^+$ ions as the counter cations, we have denoted many efforts to remove them and replace them by K$^+$ ions. However, all of the attempts to avoid lithium ion have proven unsuccessful; these include 1) by using isolated crystals of Mg−Mg-bonded compound **3** as the starting material (instead of *in-situ* generation of **3**); 2) by adding other chelating agents (such as DME and 18-crown-6) to better coordinate the potassium ion; 3) and changing solvents for better crystallinity. All

these experiments resulted in oily products which did not crystallize even at low temperatures. Nevertheless, the oil, after rinsing with toluene and small amount of THF, shows an almost identical (and better due to its good solubility) ^{1}H NMR spectrum in THF-d_8 (Fig. S7) to that of product **5** (Fig. S6). This is consistent with the formation of the $[(L^{3}Mg)_2(t\text{BuNCO})_2]^{2-}$, possibly with K^+ as counter cations (yields for this species are good, ca. 60%). More encouragingly, it was possible to measure the ^{13}C NMR of this sample, which displays the resonances of the coupled $(t\text{BuNCO})_2$ fragment (30.4 for $C(CH_3)_3$, 51.9 for $C(CH_3)_3$, and 169.1 for N*C*O; Fig. S8). In addition, by introducing lithium ions (adding the original *n*BuLi solution or LiBr salt) into the system, the Li-containing compound **5** could be isolated as crystals.

On the other hand, in repeated experiments by using *in-situ* prepared Mg−Mg-bonded compound (**3**), crystals of product **5** can be readily obtained in most cases. Therefore, we speculated that there may be some Li-containing impurities (possibly LiBr) in the system which initially originate from *n*BuLi (used in the synthesis of $PhCH_2K$) and have not been removed during the work up in the following steps. To prove this, we analyzed the synthesized $PhCH_2K$ by ICP_aes (IRIS Advantage), and the result demonstrates the presence of about 10% of Li relative to K atoms.

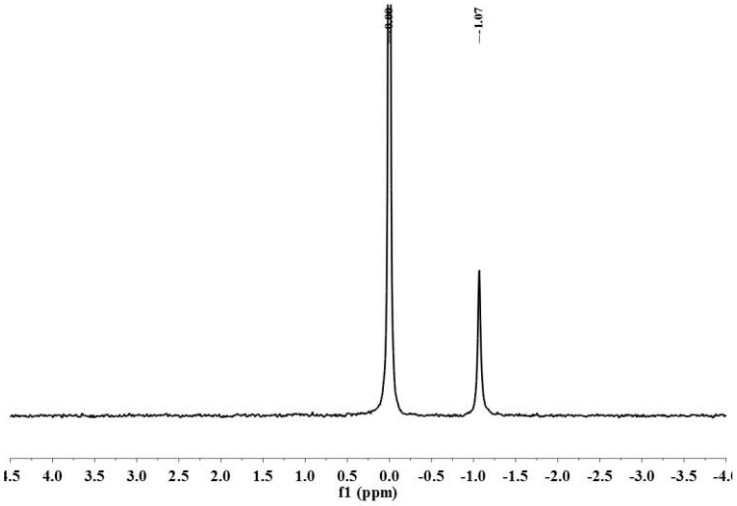


Fig. S5 ^{7}Li NMR spectrum of compound **5** (THF-d_8, 298 K), recorded on a Bruker Avance III-400 spectrometer with an external standard of 1.2 M LiCl in THF-d_8.

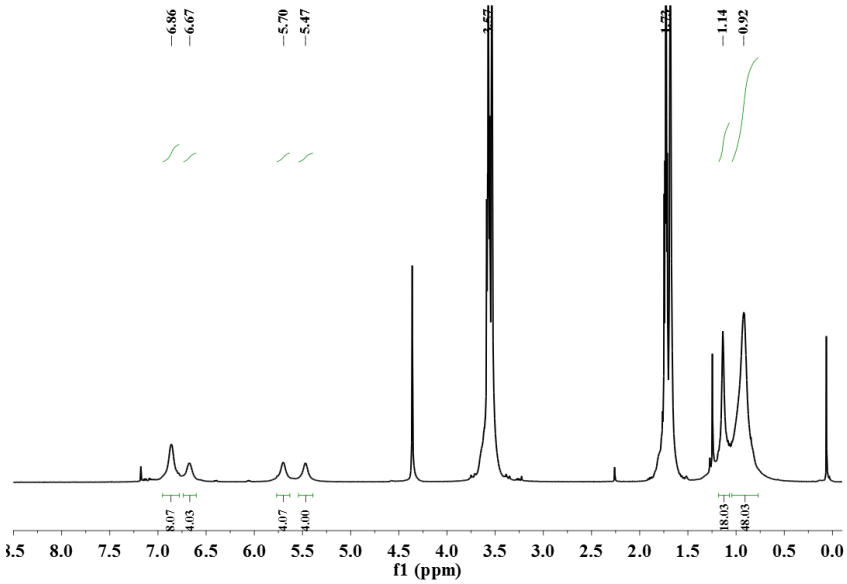


Fig. S6 ^{1}H NMR spectrum of compound **5**.

^{1}H NMR (400 MHz, THF-d_8, 298 K): δ = 0.92 (b, 48H, CH(CH_3)$_2$), 1.14 (s, 18H, C(CH_3)$_3$), 1.73 (THF), 3.57 (THF + CH(CH$_3$)$_2$), 5.47 (m, 4H, *o*-Ar-H), 5.70 (m, 4H; *m*-Ar-H), 6.67 (m, 4H; *p*-Dipp-H), 6.86 (m, 8H; *m*-Dipp-H).

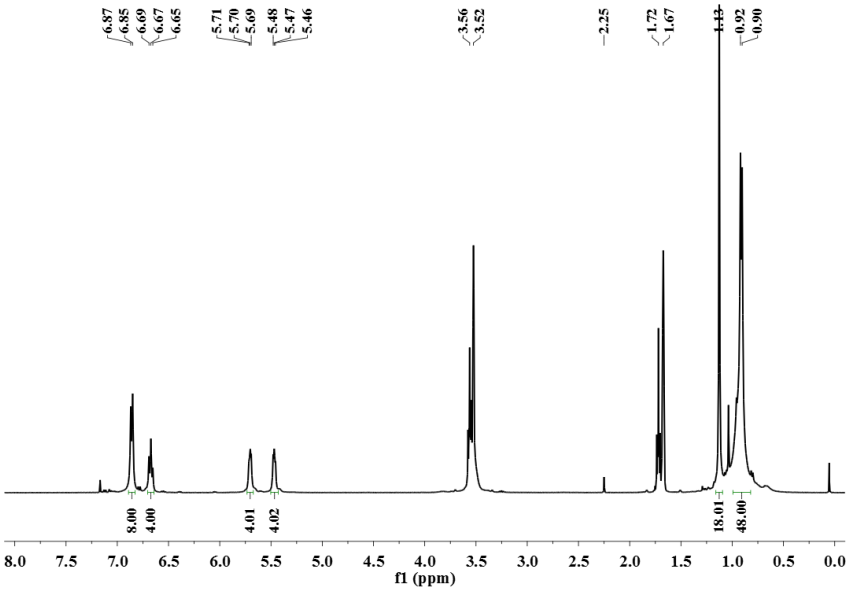


Fig. S7 ^{1}H NMR spectrum of proposed '$K_2[(L^3Mg)_2(t$BuNCO)$_2]$'.

^{1}H NMR (400 MHz, THF-d_8, 298 K): δ = 0.90 (d, J = 8.0 Hz, 48H; CH(CH_3)$_2$), 1.13 (s, 18H, C(CH_3)$_3$), 1.72 (THF),, 3.56 (THF), 3.56 (CH(CH$_3$)$_2$), 5.47 (m, 4H, *o*-Ar-H), 5.70 (m, 4H; *m*-Ar-H), 6.67 (m, 4H; *p*-Dipp-H), 6.85 (m, 8H; *m*-Dipp-H).

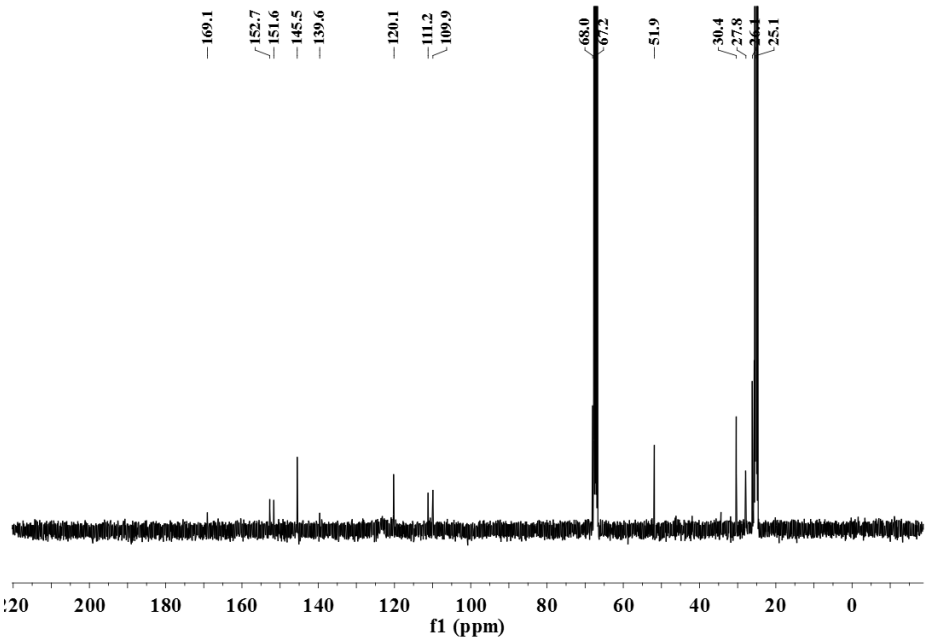


Fig. S8 ^{13}C NMR spectrum of proposed '$K_2[(L^3Mg)_2(t\text{BuNCO})_2]$'.

^{13}C NMR (100.6 MHz, THF-d_8, 298 K): 25.1 (THF), 26.1 (CH(CH_3)$_2$), 27.8 (CH(CH_3)$_2$, 30.4 (C(CH_3)$_3$), 51.9 (C(CH_3)$_3$), 67.2 (THF), 109.9 (*p*-Dipp-C), 111.2 (*m*-Ar-C), 120.1 (*m*-Dipp-C), 139.6 (*o*-Ar-C), 145.5 (*o*-Dipp-C), 151.6 (Dipp-C_{ipso}), 152.7 (Ar-C_{ipso}), 169.1 (NCO).

S2. X-ray crystallography

X-ray diffraction data for compounds **2**–**5** were collected on a Bruker SMART APEX II diffractometer at low temperature (100 K) with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption correction, structure solution, and refinement were done by using the SADABS,[S4] SHELXS-2014, and SHELXL-2014 programs.[S5] Hydrogen atoms bonded to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Crystallographic data have been deposited to the Cambridge Crystallographic Data Centre with reference numbers CCDC 1813404 (for **2**), 1813405 (**3**), 1813406 (**5**), and 1813407 (**4**).

Table S1. Crystallographic data and refinement details for compounds **2–5**.

compound	**2**	**3**	**4**	**5**
formula	$C_{50}H_{66}KMgN_2O_3$	$C_{54}H_{76}KMgN_2O_3$	$C_{92}H_{140}K_2Mg_2N_{10}O_8$	$C_{110}H_{174}Li_2Mg_2N_6O_{12}$
M*w*	806.45	864.57	1640.95	1835.04
crystal system	Triclinic	Orthorhombic	Triclinic	Triclinic
space group	*P*-1	*Pbca*	*P*-1	*P*-1
a (Å)	12.886(2)	20.745(3)	9.703(3)	12.575(2)
b (Å)	12.993(2)	16.854(3)	13.489(4)	12.681(2)
c (Å)	16.345(3)	28.794(5)	19.372(5)	17.464(3)
α (°)	78.553(3)	90	104.191(3)	80.066(2)
β (°)	71.205(2)	90	92.282(3)	81.603(2)
γ (°)	62.174(2)	90	110.287(3)	84.333(2)
V (Å^3)	2287.4(7)	10067(3)	2283.9(11)	2706.1(9)
Z	2	8	1	1
D_{calc} /g cm^{-3}	1.169	1.141	1.193	1.126
F(000)	868	3752	888	1002
μ /mm^{-1}	0.172	0.161	0.177	0.082
θ range	1.931-25.288	1.710-25.292	1.675-24.993	1.635-25.108
total reflns	7982	9049	7652	9244
unique reflns	5671	6745	6002	7118
R(int)	0.0409	0.0525	0.0410	0.0406
R_1, wR_2 [$I > 2\sigma(I)$]	0.0469, 0.1207	0.0623, 0.1629	0.0592, 0.1472	0.0710, 0.1629
R_1, wR_2 (all data)	0.0738, 0.1330	0.0855, 0.1821	0.0749, 0.1567	0.0889, 0.1729
GOF (F^2)	1.014	1.116	1.053	1.028

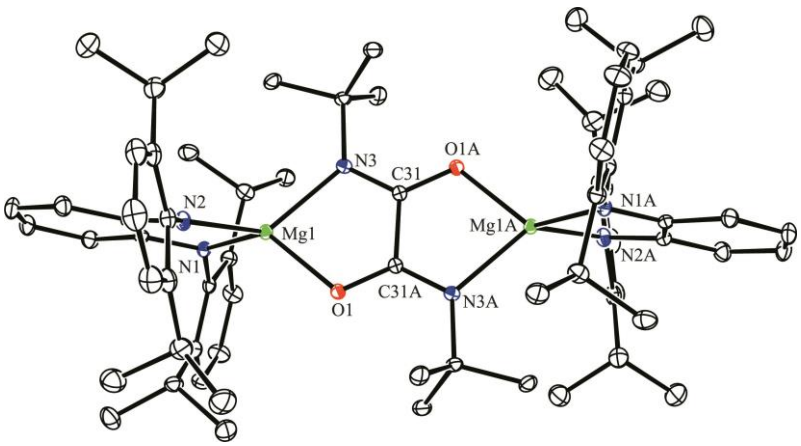
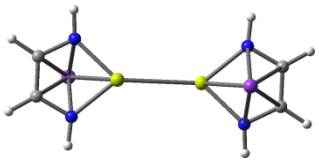
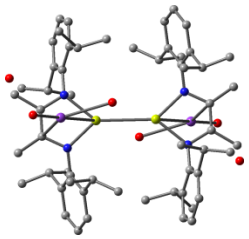


Fig. S9 Molecular structure of the anionic complex [**L**^{3}Mg{(*t*BuN)C(O)C(O)N(*t*Bu)}Mg**L**^{3}]$^{2-}$ in product **5** with 30% probability thermal ellipsoids. Hydrogen atoms, solvent molecules and Li(THF)$_4^+$ cations have been omitted for clarity. Selected bond distance (Å) and angles (º): Mg1−N1, 2.026(2); Mg1−N2, 2.026(2); Mg1−O1, 1.9847(19); Mg1−N3, 2.120(2); O1−C31A, 1.289(3); C31−C31A, 1.537(5); C31−N3, 1.302(3); N1−Mg1−N2, 84.76(9); O1−Mg1−N3, 81.21(8).

S3. Computational details

The structure optimization and NBO bonding analysis for the model compounds $[K(H_2O)_3]_2[L^2Mg{-}MgL^2]$ (**2'**), $[K(H_2O)_3]_2[L^3Mg{-}MgL^3]$ (**3'**), $[L'Mg(H_2O)_2K(H_2O)(\mu\text{-}N_3)_2K(H_2O)Mg(H_2O)_2L']$ (**4'**), and $[Li(H_2O)_4]_2[(L'Mg)_2(t\text{BuNCO})_2]L']$ (L' = N,N'-Ph_2-*o*-phenylenediamine (**5'**) were carried out at the DFT (B3LYP) level with a 6-311g* basis set using the Gaussian 09 program.[S6] The B3LYP method is a hybrid of the HF and DFT methods, incorporating Becke's three-parameter exchange functional (B3)[S7] with the Lee, Yang, and Parr (LYP) correlation functional. Bonding analyses were performed by means of natural bond orbital (NBO) analysis and natural population analysis (NPA). Wiberg bond indices (WBI) were evaluated with Weinhold's natural bond orbital method.[S8] The excited states were computed by TD-DFT method combined with implicit solvation model[S9] at the optimized ground state geometries. CAM-B3LYP functional[S10] was employed to improve the long range behavior of XC functionals. The basis sets were extended to 6-311G* triple-zeta.

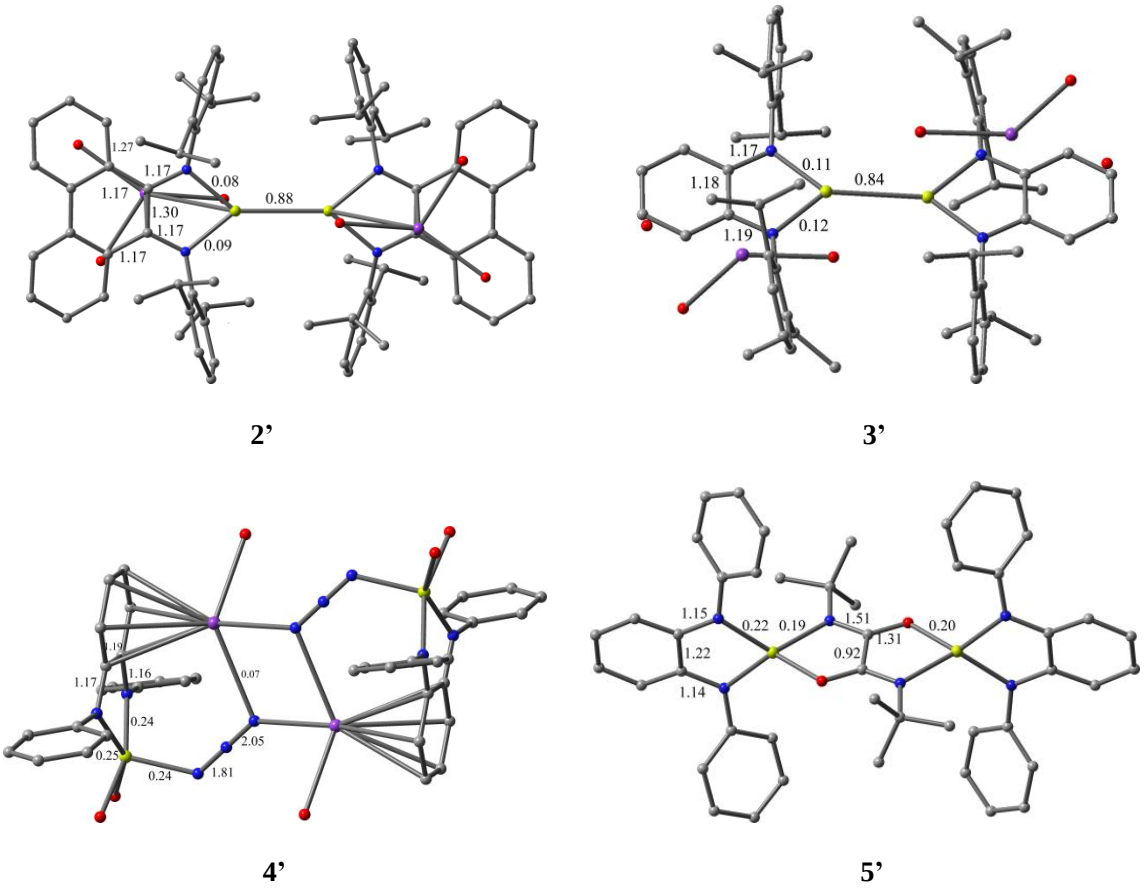
Table S2. Orbital composition of the Mg−Mg bond in compound **1** reported previously* by using a simplified model and full molecule, respectively, with different DFT methods.

Model Compound / Orbital Composition		
B3LYP /6-311G*	43.5% s, 56.2% p, 0.2% d	81.7% s, 17.7% p, 0.6% d
B3LYP/dzp	44.8% s, 55.0% p, 0.2% d	Optimized structure distortion
B3PW91/6-311+G(d)	45.2% s, 54.6% p, 0.2% d	74.0%s, 25.6% p, 0.4% d

* see Ref. [S11].

Table S3. Natural charges of the model compounds **2'**−**5'**.

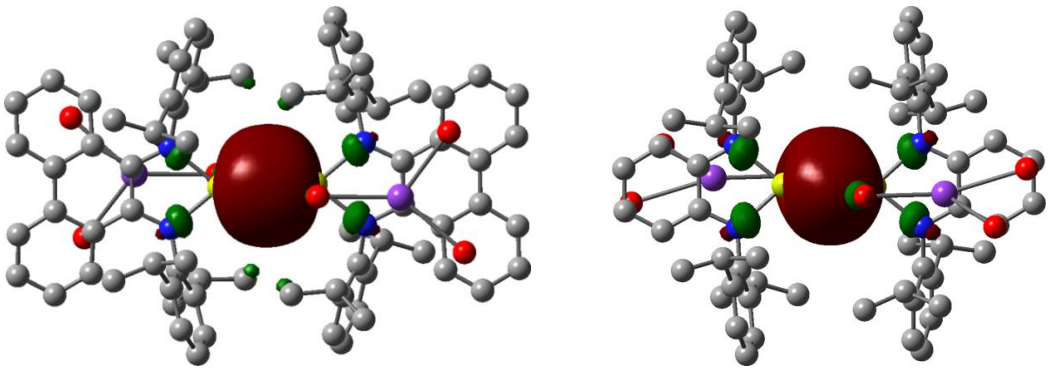
	2'	**3'**	**4'**	**5'**
Mg	0.71	0.73	1.33	1.45
L	−1.68	−1.63	−1.60	−1.71
Small molecule			−0.74	−1.48



2’ **3’**

4’ **5’**

Fig. S10 Optimized structures of **2’**–**5’** labelled with selected bond orders.



HOMO−2 HOMO−2

Fig. S11 The Mg−Mg bonding orbital of the model compounds **2’** (left) and **3’** (right).

S4. UV-Vis and fluorescence studies

UV−Vis measurements were performed on a Cary-100 spectrophotometer, and fluorescence spectra were recorded on a Horiba Fluorolog-3 spectrometer, using cuvettes from Ajilent Technologies (for $\mathbf{L}^{2}$ and **2**: THF solution, 2×10^{-4} mol/L; for $\mathbf{H_2L}^{3}$ and **3**: THF solution, 2.4×10^{-5} mol/L).

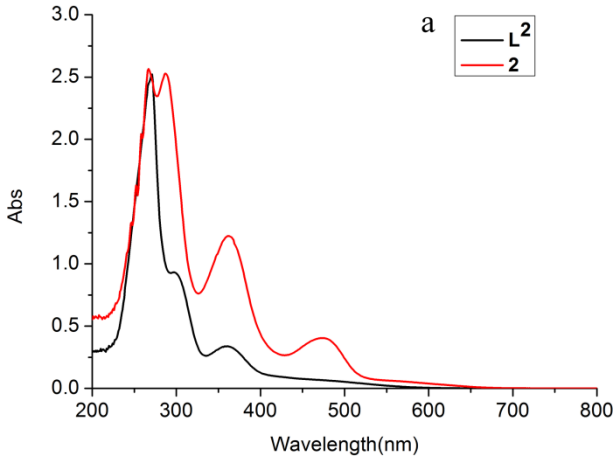


Fig. S12 UV-Vis spectra of $\mathbf{L}^2$ (black) and **2** (red) in THF at room temperature.

The absorption spectra of ligand $\mathbf{L}^2$ and the corresponding Mg−Mg compound **2** (collected in THF, Fig. S8) are similar in the higher-energy region, with dominant peaks at about 260 and 290 nm and a weaker band at ca. 360 nm. These absorptions are assigned to ligand-based transitions. However, molecule **2** has an additional weak band centered at 481 nm, which is expected to involve the Mg−Mg bond.

To assist assignment of the electronic transitions, TD-DFT computations were conducted at the B3LYP/6-311G* level on model compound **2'**, $[K(H_2O)_3]_2[\mathbf{L}^2Mg{-}Mg\mathbf{L}^2]$. Despite many allowed transitions with non-neglectable amplitudes, the structure of the experimental spectra was re-produced by simulation (Fig. S11). The first two theoretical bands at 273 and 286 nm correspond to the experimental 260 and 290 nm absorptions, respectively. The largest contribution to the third band is the 327 nm (experimental 360 nm) absorption. The new, lowest-energy band (experimental 481 nm) is of particular interest, and computations show that it consists of contributions from several states (Table S4 and Fig. S9). The stronger peak at 456 nm involves ligand-to-ligand transitions, while the weaker one at 415 nm corresponds to an excitation from the Mg−Mg σ bond (HOMO−2) to the low-lying Mg−Mg π orbital (LUMO+2).

To validate the calculations at the B3LYP/6-311G* level of theory, another method (CAM-B3LYP with the basis set 6-311G*) was also used for the TD-DFT. The theoretical bands at 279, 287 and 321 nm are consistent with the experimental absorptions at 260, 290 and 360 nm. There are several states supporting the experimental band at 481 nm (Table S5 and Fig. S12). The peaks at 459 and 413 nm involves ligand-to-ligand transitions, while the weaker one at 382 nm corresponds to an excitation from the Mg−Mg σ bond to the Mg−Mg π orbital (HOMO−2→LUMO+2 and HOMO−2→LUMO+6), indicating the facile transition of the metal−metal bonding electrons under UV-Vis irradiations.

Similarly, the absorption spectrum of the pda compound **3** (in THF, Fig. S9) also shows a new feature (at 410 nm). TD-DFT computations (B3LYP/6-311G*, Fig. S15) reveal that the new absorption appears as a broad band composed of two transitions (Table S6 and Fig. S14). Both of them involve the metal−metal bond, wherein the stronger one (427 nm) is a transition from Mg−Mg σ bond (HOMO−2) to the empty Mg−Mg π orbital (LUMO), while the weaker one (475 nm) is due to the ligand π (HOMO) to Mg−Mg π (LUMO) transition.

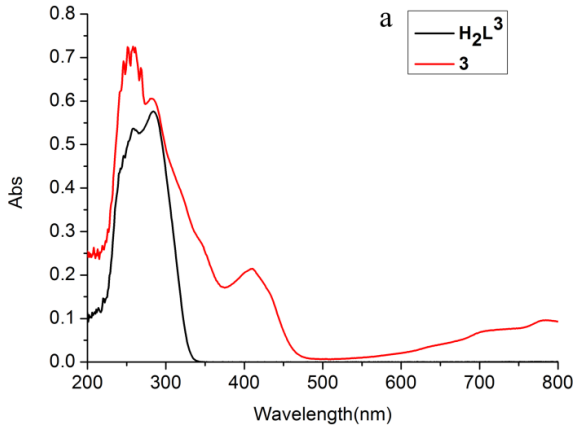
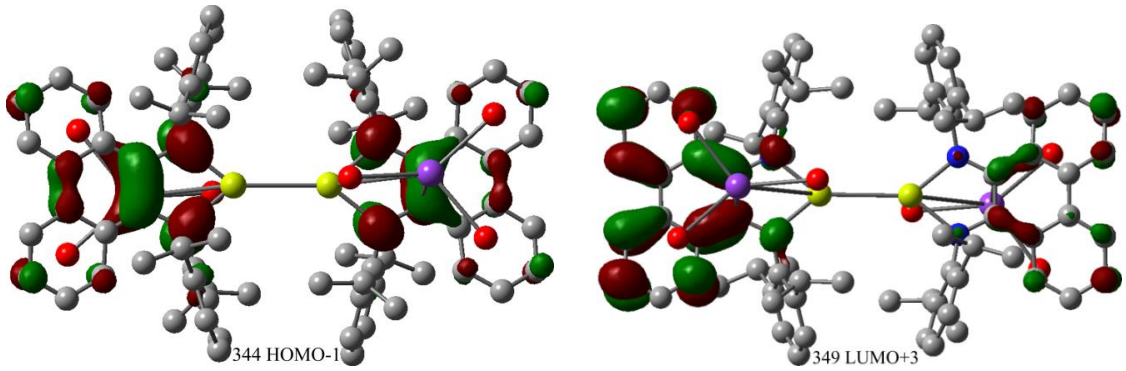


Fig. S13 UV-Vis spectra of $\mathbf{H_2L^3}$ (black) and **3** (red) in THF at room temperature.

Table S4. Absorption wavelengths, oscillator strengths, main transition pairs and amplitudes for selected excited states of compound **2′** at the B3LYP/6-311G* level of theory.

wavelength [nm]	*f*	transition	excitation amplitudes[a]	assignment
455.58	0.4503	344 HOMO–1 => 349 LUMO+3	-0.41080	Ligand π→ Ligand π*
		345 HOMO => 350 LUMO+4	0.47248	
414.90	0.1136	343 HOMO–2 => 348 LUMO+2	0.63987	Mg–Mg σ → Mg–Mg π

[a] Only those excitation amplitudes greater than 0.3 are shown.



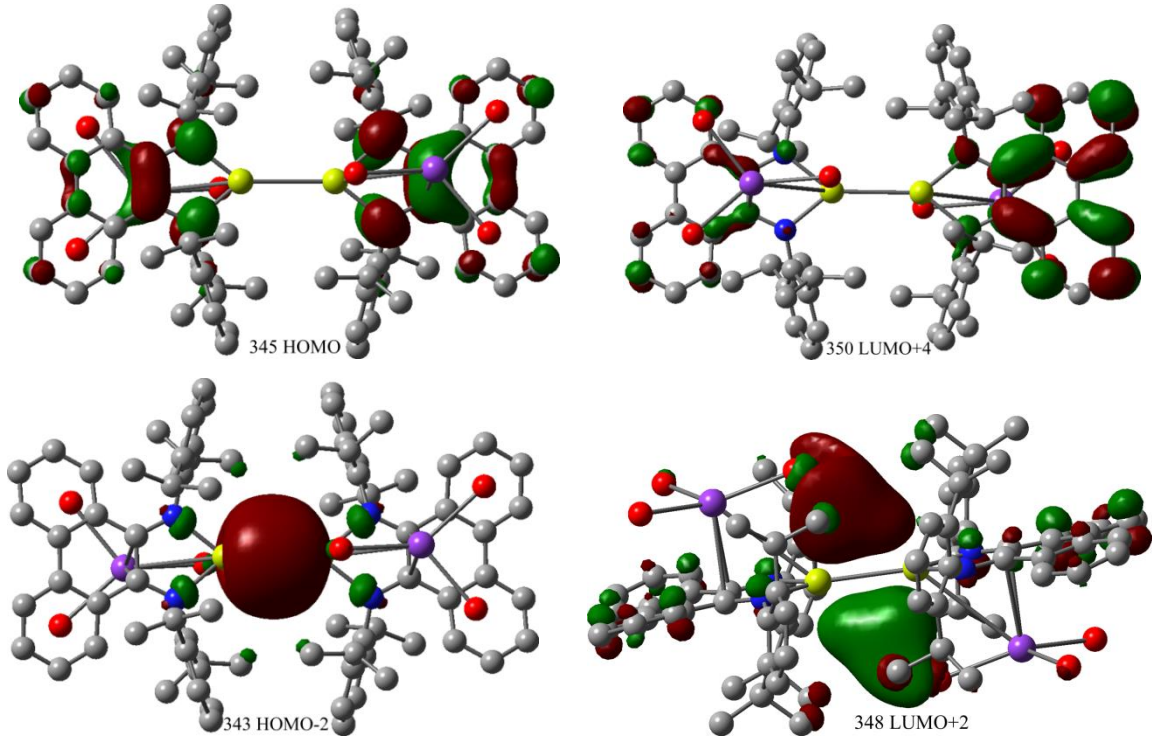


Fig. S14 Visualization of the donor/acceptor orbitals for the major theoretical vertical excitations for **2′** (B3LYP/6-311G*). Frontier orbitals in the UV-Vis spectra simulation at the B3LYP/6-311G* level of theory. Isovalue = 0.004.

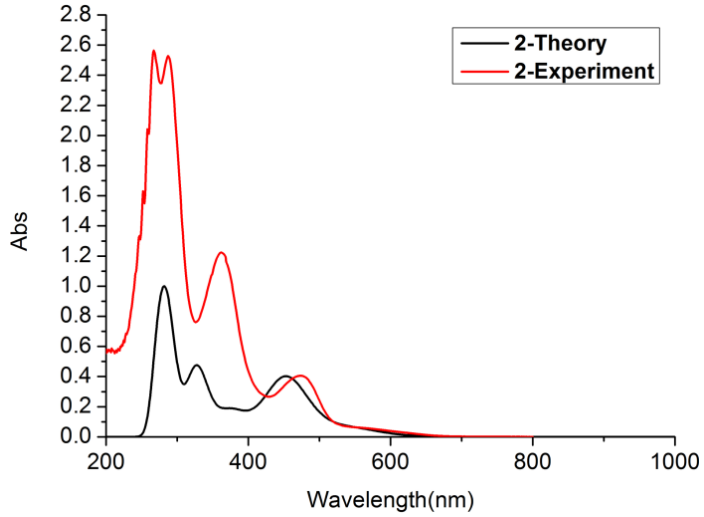
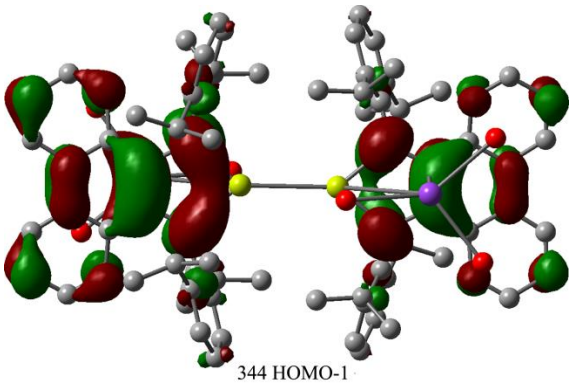


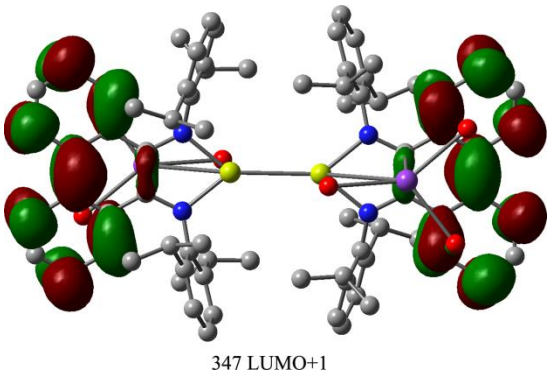
Fig. S15 Comparison of the experimental and computational (B3LYP/6-311G*) UV/Vis spectra of **2**.

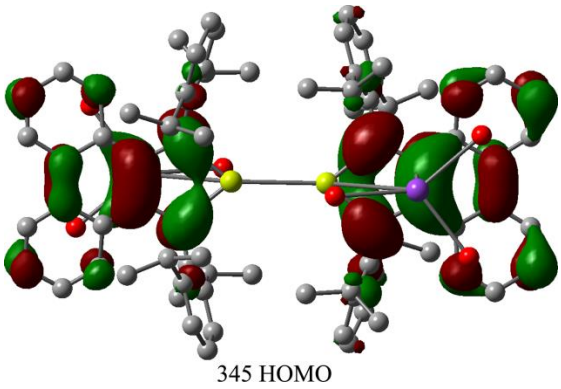
Table S5. Absorption wavelengths, oscillator strengths, main transition pairs and amplitudes for selected excited states of compound **2′** at the CAM-B3LYP/6-311G* level of theory.

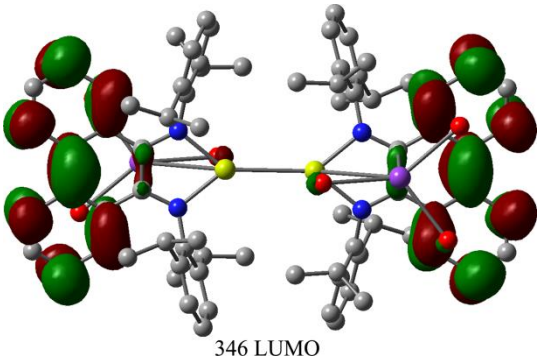
wavelength [nm]	*f*	transition	excitation amplitudes[a]	assignment
459.35	0.1730	344 HOMO–1 => 347 LUMO+1	-0.47491	Ligand π→ Ligand π*
		345 HOMO => 346 LUMO	0.45785	Ligand π→ Ligand π*
413.00	0.6329	344 HOMO–1 => 349 LUMO+3	-0.41601	Ligand π→ Ligand π*
		345 HOMO => 350 LUMO+4	0.47129	Ligand π→ Ligand π*
382.12	0.1986	343 HOMO–2 => 348 LUMO+2	0.43934	Mg–Mg σ→Mg–Mg π
		343 HOMO–2 => 352 LUMO+6	0.41241	Mg–Mg σ→Mg–Mg π

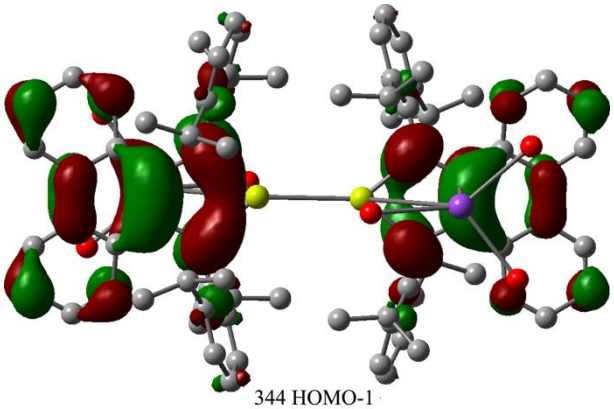
[a] Only those excitation amplitudes greater than 0.3 are shown.

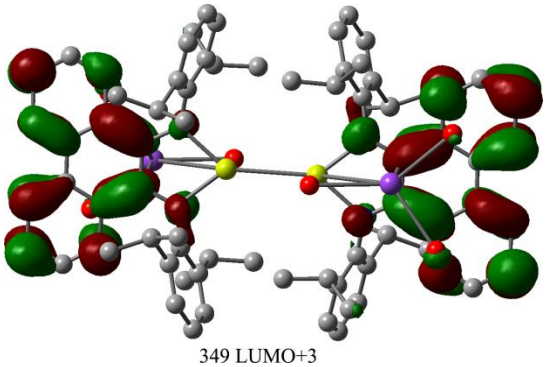












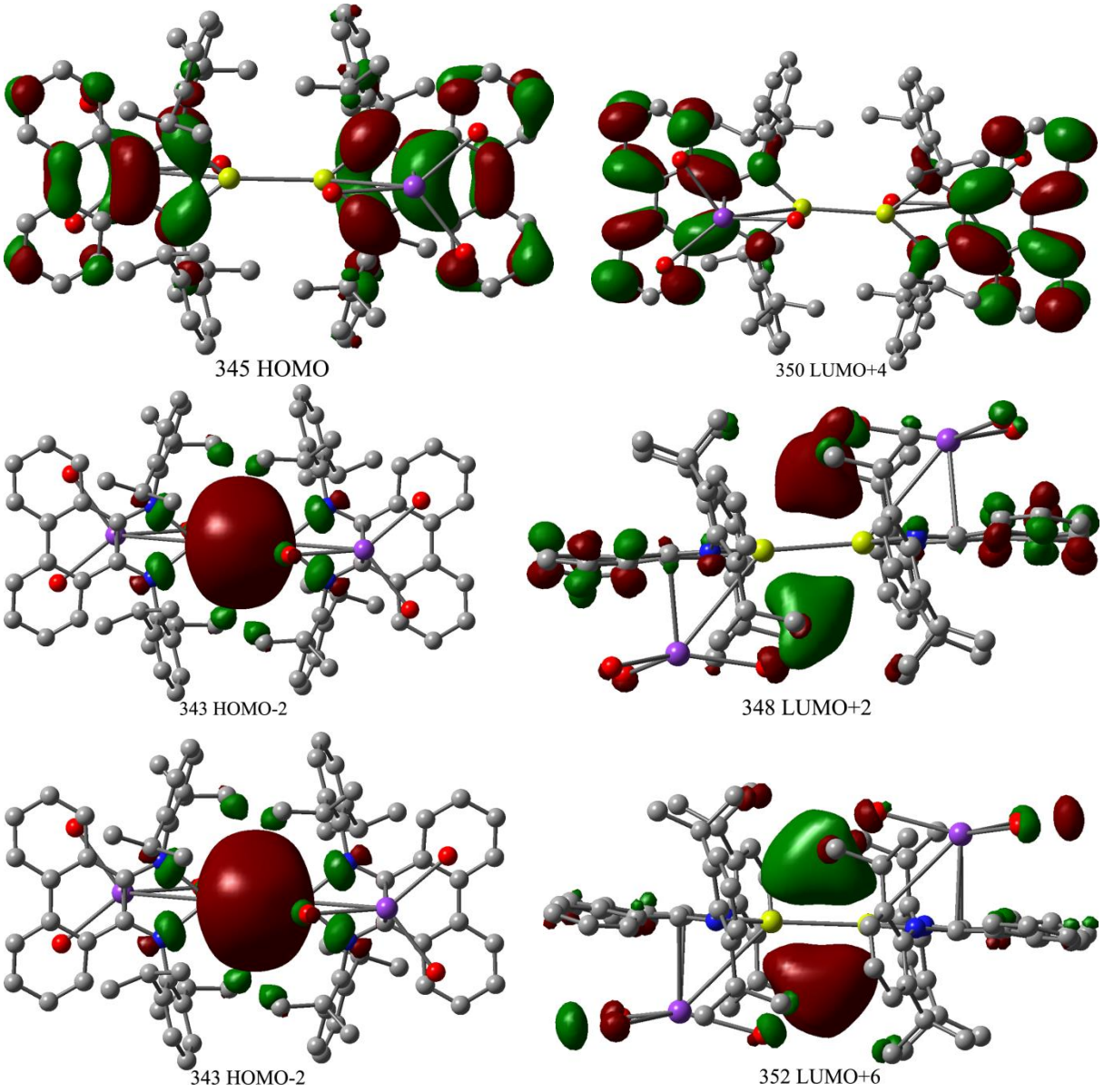


Fig. S16 Visualization of the donor/acceptor orbitals for the major theoretical vertical excitations for **2'** at the CAM-B3LYP/6-311G* level of theory. Frontier orbitals in the UV-Vis spectra simulation at the CAM-B3LYP/6-311G* level of theory for **2'**. Isovalue = 0.004.

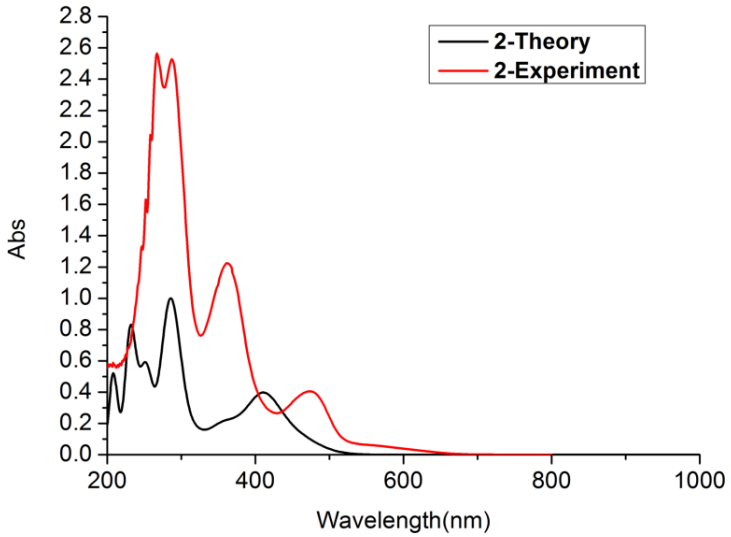
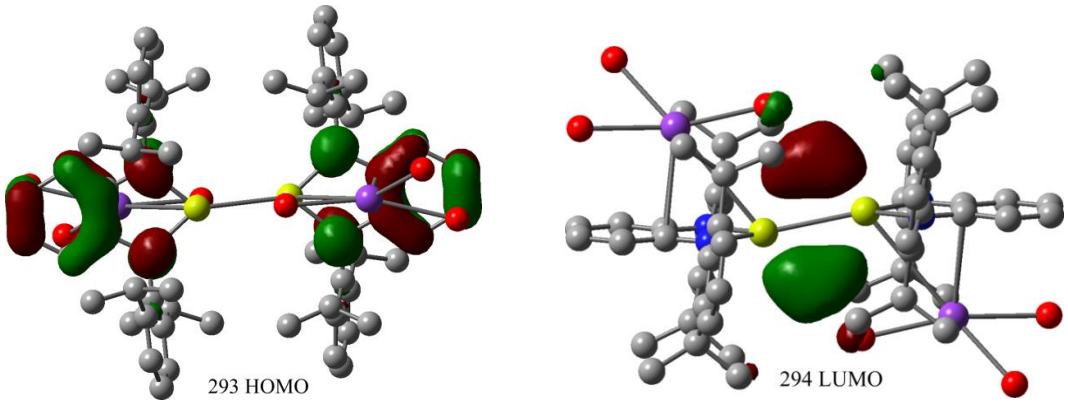


Fig. S17 Comparison of experimental and computational (CAM-B3LYP/6-311G*) UV-Vis spectra of **2**.

Table S6. Absorption wavelengths, oscillator strengths, main transition pairs and amplitudes for selected excited states of compound **3'** at the B3LYP/6-311G* level of theory.

wavelength [nm]	*f*	transition	excitation amplitudes[a]	assignment
474.64	0.1034	293 HOMO = > 294 LUMO	0.69767	Ligand π → Mg–Mg π
427.44	0.2059	291 HOMO–2 = > 294 LUMO	0.69647	Mg–Mg σ → Mg–Mg π

[a] Only those excitation amplitudes greater than 0.3 are shown.



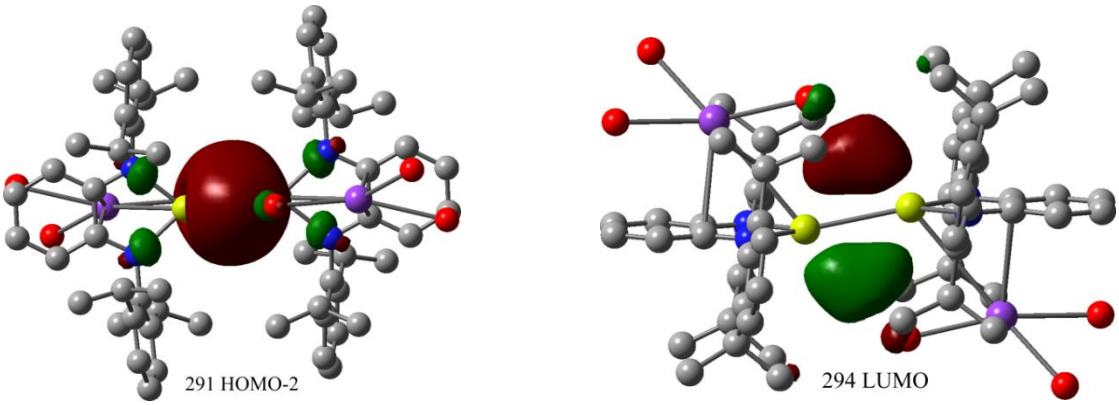


Fig. S18 Visualization of the donor/acceptor orbitals for the major theoretical vertical excitations for **3** **(**B3LYP/6-311G*). Frontier orbitals in the UV-Vis spectra simulation at the B3LYP/6-311G* level of theory for **3'**. Isovalue = 0.004.

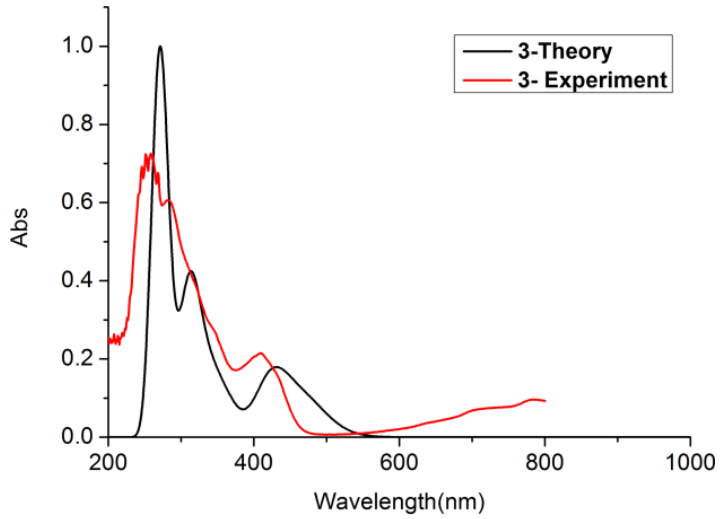


Fig. S19 Comparison of the experimental and computational (B3LYP/6-311G*) UV-Vis spectra of **3**.

Table S7. Absorption wavelengths, oscillator strengths, main transition pairs and amplitudes for selected excited states of compound **3'**at the CAM-B3LYP/6-311G* level of theory.

wavelength [nm]	*f*	transition	excitation amplitudes[a]	assignment
398.80	0.2638	291 HOMO–2 = > 294 LUMO	0.54906	Ligand π→ Mg–Mg π
		293 HOMO = >294 LUMO	0.32724	Mg–Mg σ→Mg–Mg π

[a] Only those excitation amplitudes greater than 0.3 are shown

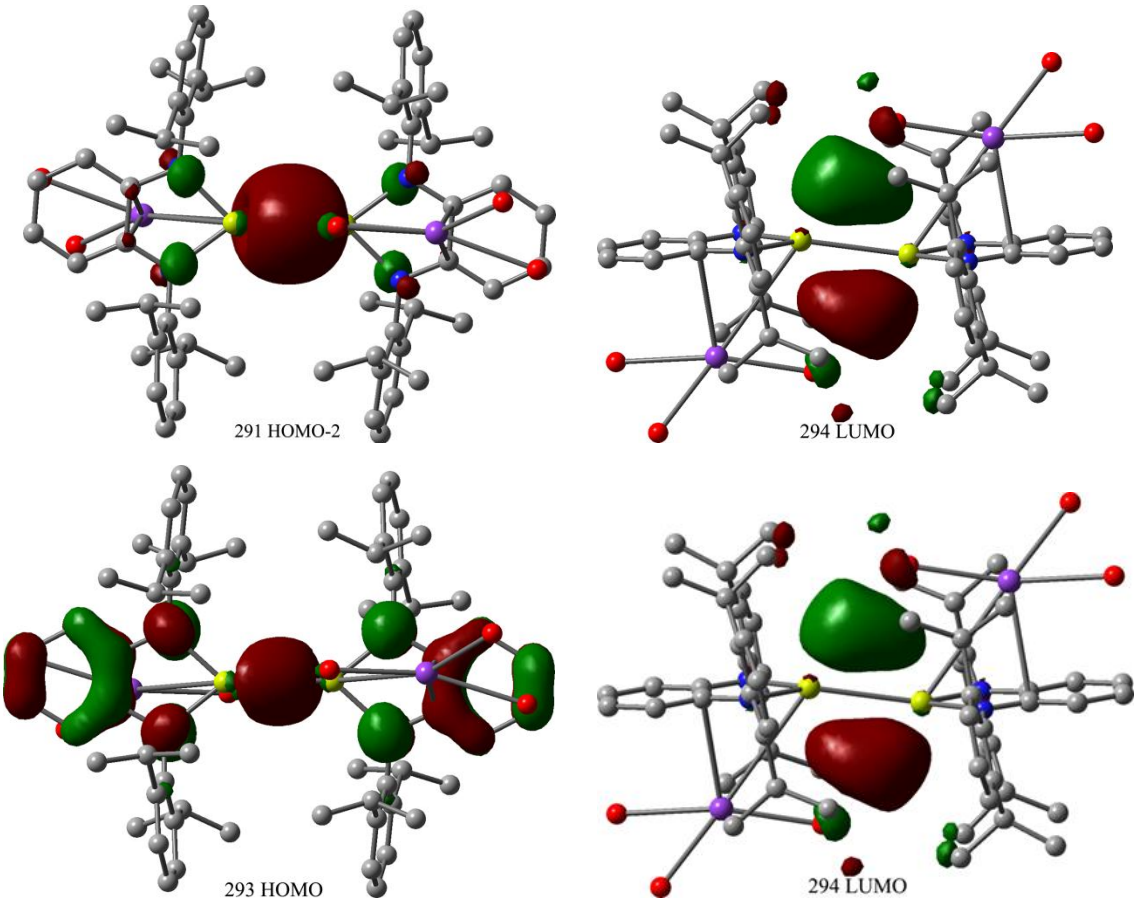


Fig. S20 Visualization of the donor/acceptor orbitals for the major theoretical vertical excitations for **3** at the CAM-B3LYP/6-311G* level of theory. Frontier orbitals in the UV-Vis spectra simulation at the CAM-B3LYP/6-311G* level of theory for **3'**. Isovalue = 0.004.

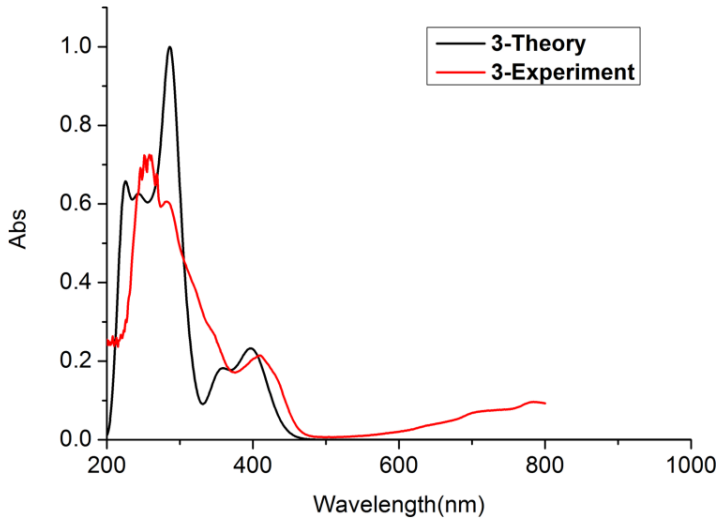


Fig. S21 Comparison of the experimental and computational (CAM-B3LYP /6-311G*) UV-Vis spectra of compound **3**.

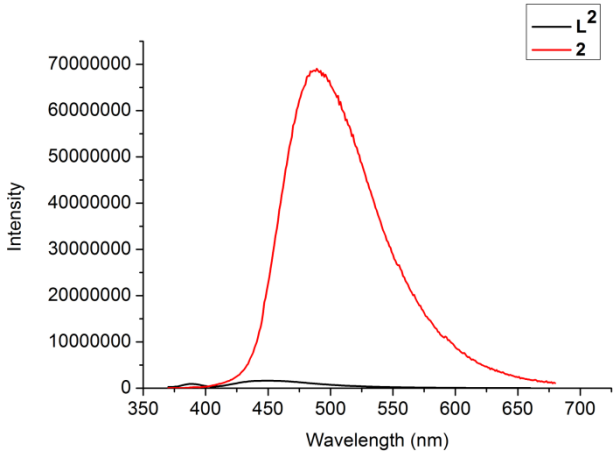


Fig. S22 Emission spectra of $\mathbf{L}^2$ (black) and **2** (red) in THF at room temperature (λ_{ex} = 350 nm).

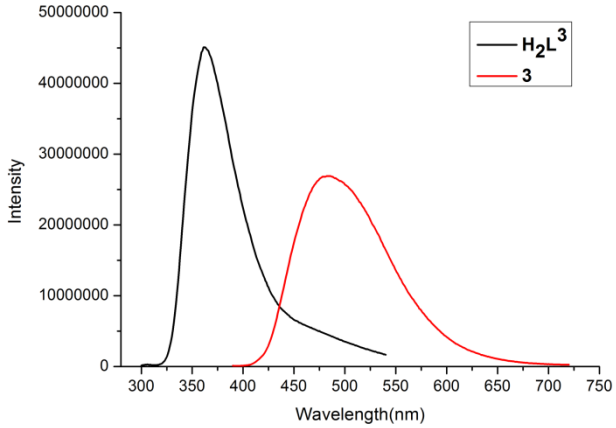


Fig. S23 Emission spectra of $\mathbf{H_2L}^3$ (black) and **3** (red) in THF at room temperature (λ_{ex} = 280 nm for $\mathbf{H_2L}^3$ and 370 nm for **3**).

Table S8. The emission wavelength, oscillator strength, main transition pair and its amplitude for the first excited state of compound **3'** at the CAM-B3LYP/6-311G* level of theory.

wavelength [nm]	*f*	transition	amplitudes[a]	assignment
536.83	0.4301	294 LUMO = > 293 HOMO	-0.64566	Mg–Mg π → Mg–Mg σ

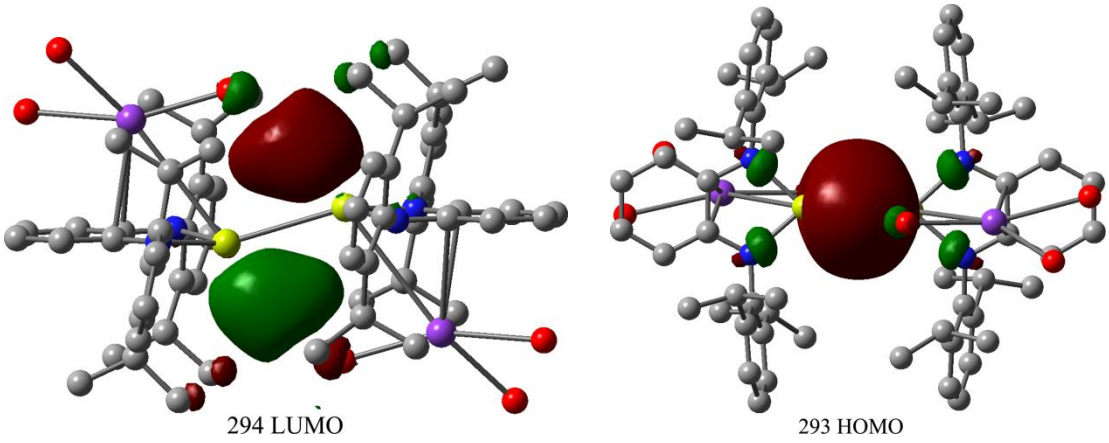


Fig. S24 Visualization of the donor/acceptor orbitals for the major theoretical vertical excitations for **3** at the CAM-B3LYP/6-311G* level of theory. Frontier orbitals in the fluorescence spectra simulation at the CAM-B3LYP/6-311G* level of theory for **3'**. Isovalue = 0.004.

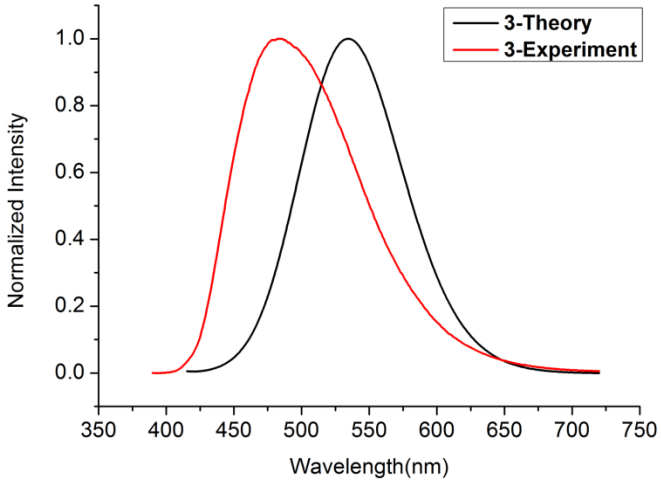


Fig. S25 Comparison of the experimental and computed (CAM-B3LYP/6-311G*) emission spectra of **3**.

Table S9. Cartesian coordinates of the optimized geometry for **2'**

K	-4.20038100	0.27948100	-2.83485200	C	-2.38124800	3.61055700	-0.42553100
Mg	-1.51296700	-0.01161700	0.02268800	C	-3.10317300	3.05535600	1.84633200
N	-3.11845700	-1.34673200	0.05398600	C	-5.64178800	1.40223700	0.09027600
N	-3.12260500	1.31814300	0.06808600	C	-3.08339800	-3.09523700	1.81817400
O	-6.37975900	1.80395500	-3.17874800	C	-5.63711400	-1.43858700	0.06694600
O	-5.57480100	-1.96226800	-3.25816800	C	-2.11403700	4.91296300	0.00186900
O	-1.58539700	0.05975000	-3.51533600	H	-1.72839700	5.63687600	-0.70999400
C	-2.89417100	2.65326800	0.49598200	C	-2.41100100	-3.64369800	-0.47042300
C	-4.36578400	-0.73035600	0.11577200	C	-2.18406700	3.27855800	-1.90138900
C	-4.36932200	0.69739000	0.13231000	H	-2.42020400	2.21806000	-2.00598900

C	-5.73125700	2.80780800	-0.14041700	H	-0.60852300	3.17650200	-3.40824500
H	-4.83538000	3.37794400	-0.31322800	H	-0.03569500	2.89532200	-1.74983100
C	-2.80436000	-4.41520300	2.17942200	C	-2.51412100	-1.94722700	4.00447000
H	-2.95921300	-4.72572700	3.20874800	H	-2.27080500	-2.88946400	4.50347600
C	-2.83736200	4.37556300	2.21629000	H	-2.87069800	-1.25073700	4.76859200
H	-3.01083800	4.68144400	3.24411300	H	-1.58556000	-1.54335600	3.59059500
C	-2.28143200	-3.30610900	-1.95196800	C	-4.91026700	-2.59000600	3.52176600
H	-2.76514300	-2.33574900	-2.08514900	H	-5.67850900	-2.72198600	2.75814700
C	-3.59451000	2.09239600	2.92455300	H	-5.27191000	-1.84489100	4.23758300
H	-3.75787000	1.12135900	2.45755600	H	-4.80749400	-3.53755900	4.06001500
C	-2.34852600	5.30929900	1.31142800	C	-3.01611400	-4.31192600	-2.85786400
H	-2.15076100	6.33013700	1.62396600	H	-2.54370100	-5.29767200	-2.84781700
C	-2.11810700	-4.94277000	-0.04940200	H	-3.00929200	-3.96644500	-3.89814100
H	-1.74127600	-5.66388800	-0.76846200	H	-4.05553600	-4.44957000	-2.54754800
C	-2.89483500	-2.68699200	0.46735000	C	-8.07731900	-1.49128200	0.32978800
C	-6.88218500	0.70063400	0.24609200	H	-9.01170100	-0.97929700	0.52118800
C	-2.32078100	-5.34136400	1.26467400	C	-8.11473100	-2.85721400	0.15445600
H	-2.10466400	-6.35990800	1.57243300	H	-9.05503800	-3.39428700	0.22276600
C	-5.72516200	-2.84305800	-0.17565200	C	-4.93402200	2.53222200	3.54371300
H	-4.82808900	-3.40636200	-0.36508700	H	-4.83553100	3.47572800	4.08980800
C	-3.57325300	-2.14025400	2.90408100	H	-5.29369800	1.78015700	4.25324300
C	-6.87844100	-0.74465000	0.24739400	H	-5.70190100	2.66749500	2.78045600
C	-6.93104500	3.48989200	-0.13706400	K	4.20028800	-0.27964700	2.83506900
H	-6.93495500	4.56152500	-0.31159900	Mg	1.51326200	0.01140900	-0.02275800
C	-6.92012300	-3.53277600	-0.13812700	N	3.11861900	1.34666400	-0.05325500
H	-6.92299000	-4.60416100	-0.31538900	N	3.12287000	-1.31824700	-0.06860300
C	-3.14259600	4.07057300	-2.81177800	O	6.37789200	-1.80683800	3.17581300
H	-2.96101300	5.14669400	-2.74023800	O	5.57310200	1.96220600	3.26064800
H	-4.19081100	3.89952300	-2.55508600	O	1.58484400	-0.06149500	3.51589500
H	-3.00699600	3.78806600	-3.86169600	C	2.89416600	-2.65312300	-0.49708800
C	-2.53558700	1.89788700	4.02513100	C	4.36595100	0.73027600	-0.11523600
H	-1.60269100	1.50638400	3.61009400	C	4.36956800	-0.69745100	-0.13274000
H	-2.88811100	1.19227800	4.78291200	C	2.38180500	-3.61094700	0.42419300
H	-2.30197800	2.83815700	4.53264200	C	3.10229800	-3.05444200	-1.84780200
C	-8.08957700	1.43761800	0.28641700	C	5.64209500	-1.40225500	-0.09196000
H	-9.02655600	0.91686900	0.43626600	C	3.08465600	3.09608200	-1.81663200
C	-8.13184900	2.80360200	0.10998900	C	5.63721000	1.43853200	-0.06534700
H	-9.07817800	3.33340900	0.14458600	C	2.11446400	-4.91314200	-0.00375700
C	-0.81517700	-3.17440200	-2.38917900	H	1.72926300	-5.63746000	0.70793400
H	-0.28678400	-2.42287100	-1.79614400	C	2.41054900	3.64330500	0.47176600
H	-0.73879000	-2.90944000	-3.45254400	C	2.18534500	-3.27975500	1.90032000
H	-0.26576600	-4.10956400	-2.25985200	H	2.42138100	-2.21928500	2.00535600
C	-0.73267200	3.47356900	-2.35940200	C	5.73174800	-2.80811800	0.13690400
H	-0.41818400	4.51693600	-2.29120800	H	4.83599300	-3.37850400	0.30952800

C	2.80562000	4.41617600	-2.17741700	H	0.26406900	4.10802800	2.25999100
H	2.96114700	4.72723600	-3.20647900	C	0.73422300	-3.47525200	2.35897100
C	2.83641500	-4.37447400	-2.21832100	H	0.41993300	-4.51866300	2.29054200
H	3.00931000	-4.67977800	-3.24641300	H	0.61053800	-3.17865800	3.40801300
C	2.28009900	3.30510200	1.95309600	H	0.03677900	-2.89694200	1.74999000
H	2.76391400	2.33479300	2.08626700	C	2.51704600	1.94933700	-4.00400500
C	3.59285600	-2.09079400	-2.92575300	H	2.27401100	2.89185500	-4.50262300
H	3.75639700	-1.12002300	-2.45825600	H	2.87424000	1.25335100	-4.76830100
C	2.34825700	-5.30876100	-1.31366000	H	1.58822700	1.54515400	-3.59103600
H	2.15044900	-6.32946100	-1.62662100	C	4.91278000	2.59208600	-3.51924100
C	2.11767800	4.94251800	0.05115900	H	5.68049000	2.72364500	-2.75501600
H	1.74021700	5.66321500	0.77030900	H	5.27498200	1.84747100	-4.23529600
C	2.89516700	2.68711000	-0.46614100	H	4.81027400	3.53997700	-4.05694500
C	6.88240200	-0.70037700	-0.24732500	C	3.01400000	4.31075300	2.85981800
C	2.32116300	5.34178600	-1.26258000	H	2.54139200	5.29640600	2.84981200
H	2.10504600	6.36043200	-1.57000100	H	3.00657300	3.96489100	3.89996300
C	5.72500500	2.84270900	0.17898400	H	4.05359400	4.44870300	2.55022400
H	4.82775800	3.40568000	0.36860600	C	8.07752100	1.49171500	-0.32686600
C	3.57538800	2.14179600	-2.90276500	H	9.01208800	0.98002600	-0.51813500
C	6.87861300	0.74491800	-0.24632000	C	8.11477000	2.85741000	-0.14966000
C	6.93155900	-3.49015700	0.13191500	H	9.05511600	3.39459100	-0.21656000
H	6.93560400	-4.56201600	0.30505100	C	4.93202200	-2.53006100	-3.54604200
C	6.91993500	3.53256100	0.14298500	H	4.83330500	-3.47320700	-4.09272000
H	6.92263900	4.60373400	0.32153700	H	5.29117200	-1.77747500	-4.25528500
C	3.14446900	-4.07215700	2.80974300	H	5.70039100	-2.66576700	-2.78335200
H	2.96304000	-5.14826500	2.73757300	H	-3.74151100	-1.16720900	2.44308500
H	4.19251700	-3.90070500	2.55268000	H	3.74344100	1.16848400	-2.44227200
H	3.00932500	-3.79035600	3.85991000	H	5.37658800	2.75323300	3.77221900
C	2.53319200	-1.89578300	-4.02554900	H	5.89157300	2.26644300	2.39490100
H	1.60049100	-1.50468000	-3.60968300	H	7.21952400	-1.36898500	3.33950200
H	2.88509300	-1.18966100	-4.78313500	H	6.49587500	-2.33869400	2.37364700
H	2.29942500	-2.83580000	-4.53345200	H	1.09078600	0.75764400	3.38733400
C	8.08976000	-1.43730000	-0.28957900	H	0.94615600	-0.77950000	3.42744300
H	9.02661500	-0.91636700	-0.43956600	H	-0.94603100	0.77716700	-3.42704300
C	8.13216600	-2.80353100	-0.11509500	H	-1.09205800	-0.75986300	-3.38703400
H	9.07846600	-3.33329200	-0.15117700	H	-6.49779300	2.33684000	-2.37727600
C	0.81360900	3.17295000	2.38938400	H	-7.22040100	1.36329800	-3.34001800
H	0.28576400	2.42144000	1.79583200	H	-5.89212900	-2.26560200	-2.39168500
H	0.73667500	2.90762800	3.45261300	H	-5.37869300	-2.75384800	-3.76904300

Table S10. Cartesian coordinates of the optimized geometry for **3'**

Mg	0.04404700	0.81350100	-1.22736200	O	-0.07725900	-2.51503400	-2.42015700
K	-0.15517200	-0.93454600	-4.57782600	O	1.04115200	0.03553300	-7.03235500

O	-0.68241500	-2.02539100	-6.92217200	C	-4.26976400	3.52630500	-2.08756000
N	1.48253800	1.40483800	-2.55814700	H	-4.52289800	4.55072100	-1.83029100
N	-1.22342700	1.45338500	-2.72047900	C	-5.28952200	2.59598600	-2.23888600
C	0.93562900	1.92771200	-3.71617100	H	-6.32683100	2.88935700	-2.10935800
C	-0.51497400	1.94778100	-3.80745600	C	-4.96329600	1.28306600	-2.54565800
C	-1.09954100	2.42966300	-4.99222100	H	-5.75986500	0.55406200	-2.65158300
H	-2.18207800	2.45253000	-5.06085000	C	-3.63537900	0.88066100	-2.72045000
C	-0.33354600	2.92621400	-6.05583200	C	-1.86670000	4.24632300	-2.01397500
H	-0.82950000	3.32436800	-6.93599600	H	-0.89236500	3.79492400	-2.20056300
C	1.05621300	2.94355000	-5.95324500	C	-2.00755700	5.43428200	-2.98161200
H	1.66399800	3.37926400	-6.74179000	H	-1.19474500	6.15203300	-2.83087700
C	1.67411700	2.44197300	-4.79674300	H	-1.96875400	5.10165800	-4.02046800
H	2.75545600	2.47322300	-4.71590900	H	-2.95022500	5.96999500	-2.83226400
C	2.87911200	1.57034000	-2.33802200	C	-1.87260500	4.73443100	-0.55280700
C	3.77863300	0.49175000	-2.53278900	H	-1.74670500	3.90277500	0.14694200
C	5.13891800	0.67093300	-2.26196400	H	-1.06216700	5.45150300	-0.38305100
H	5.82553300	-0.15747600	-2.40895400	H	-2.81115200	5.23311400	-0.29401000
C	5.63275600	1.88609200	-1.80958100	C	-3.34721600	-0.56857900	-3.09330800
H	6.69206600	2.00730000	-1.60460800	H	-2.30603900	-0.76061000	-2.82452300
C	4.75310200	2.94430700	-1.61685900	C	-4.19385100	-1.59082100	-2.31947300
H	5.13929600	3.89329300	-1.25628900	H	-5.25013300	-1.55040000	-2.60028600
C	3.38622700	2.81344500	-1.87161700	H	-3.84668800	-2.60640400	-2.53310500
C	3.30446200	-0.85759100	-3.05572600	H	-4.13175400	-1.43580900	-1.24061900
H	2.21348400	-0.82468600	-3.04676500	C	-3.50784500	-0.78610900	-4.61150900
C	3.72438800	-2.03208800	-2.15851300	H	-2.90868700	-0.07934900	-5.19310900
H	3.39895400	-1.88142900	-1.12688700	H	-3.22567100	-1.80435400	-4.90361600
H	3.28199800	-2.96616500	-2.51873400	H	-4.54912700	-0.63732500	-4.91318500
H	4.80926400	-2.16957900	-2.14216800	Mg	-0.04404700	-0.81350100	1.22736200
C	3.76249300	-1.08854300	-4.50850700	K	0.15517200	0.93454600	4.57782600
H	4.85277800	-1.14722900	-4.57686200	O	0.07725900	2.51503400	2.42015700
H	3.35879200	-2.02666000	-4.90731400	O	-1.04115200	-0.03553300	7.03235500
H	3.43985000	-0.26748600	-5.15535700	O	0.68241500	2.02539100	6.92217200
C	2.47428900	4.01050600	-1.61893100	N	-1.48253800	-1.40483800	2.55814700
H	1.46872000	3.72528900	-1.92900700	N	1.22342700	-1.45338500	2.72047900
C	2.87493600	5.24108600	-2.45100400	C	-0.93562900	-1.92771200	3.71617100
H	2.89413700	5.00529300	-3.51686600	C	0.51497400	-1.94778100	3.80745600
H	2.15831300	6.05530200	-2.30285100	C	1.09954100	-2.42966300	4.99222100
H	3.86284900	5.61963100	-2.17086900	H	2.18207800	-2.45253000	5.06085000
C	2.41192900	4.36546600	-0.12143800	C	0.33354600	-2.92621400	6.05583200
H	3.38839700	4.67511300	0.26221300	H	0.82950000	-3.32436800	6.93599600
H	1.71301400	5.19161100	0.05046900	C	-1.05621300	-2.94355000	5.95324500
H	2.08814500	3.50932300	0.47790700	H	-1.66399800	-3.37926400	6.74179000
C	-2.59200200	1.83298100	-2.58589200	C	-1.67411700	-2.44197300	4.79674300
C	-2.92811000	3.17430400	-2.24727500	H	-2.75545600	-2.47322300	4.71590900

C	-2.87911200	-1.57034000	2.33802200	C	4.96329600	-1.28306600	2.54565800
C	-3.77863300	-0.49175000	2.53278900	H	5.75986500	-0.55406200	2.65158300
C	-5.13891800	-0.67093300	2.26196400	C	3.63537900	-0.88066100	2.72045000
H	-5.82553300	0.15747600	2.40895400	C	1.86670000	-4.24632300	2.01397500
C	-5.63275600	-1.88609200	1.80958100	H	0.89236500	-3.79492400	2.20056300
H	-6.69206600	-2.00730000	1.60460800	C	2.00755700	-5.43428200	2.98161200
C	-4.75310200	-2.94430700	1.61685900	H	1.19474500	-6.15203300	2.83087700
H	-5.13929600	-3.89329300	1.25628900	H	1.96875400	-5.10165800	4.02046800
C	-3.38622700	-2.81344500	1.87161700	H	2.95022500	-5.96999500	2.83226400
C	-3.30446200	0.85759100	3.05572600	C	1.87260500	-4.73443100	0.55280700
H	-2.21348400	0.82468600	3.04676500	H	1.74670500	-3.90277500	-0.14694200
C	-3.72438800	2.03208800	2.15851300	H	1.06216700	-5.45150300	0.38305100
H	-3.39895400	1.88142900	1.12688700	H	2.81115200	-5.23311400	0.29401000
H	-3.28199800	2.96616500	2.51873400	C	3.34721600	0.56857900	3.09330800
H	-4.80926400	2.16957900	2.14216800	H	2.30603900	0.76061000	2.82452300
C	-3.76249300	1.08854300	4.50850700	C	4.19385100	1.59082100	2.31947300
H	-4.85277800	1.14722900	4.57686200	H	5.25013300	1.55040000	2.60028600
H	-3.35879200	2.02666000	4.90731400	H	3.84668800	2.60640400	2.53310500
H	-3.43985000	0.26748600	5.15535700	H	4.13175400	1.43580900	1.24061900
C	-2.47428900	-4.01050600	1.61893100	C	3.50784500	0.78610900	4.61150900
H	-1.46872000	-3.72528900	1.92900700	H	2.90868700	0.07934900	5.19310900
C	-2.87493600	-5.24108600	2.45100400	H	3.22567100	1.80435400	4.90361600
H	-2.89413700	-5.00529300	3.51686600	H	4.54912700	0.63732500	4.91318500
H	-2.15831300	-6.05530200	2.30285100	H	-0.19576100	-3.44127200	-2.18204300
H	-3.86284900	-5.61963100	2.17086900	H	-0.02616700	-2.01766400	-1.58251300
C	-2.41192900	-4.36546600	0.12143800	H	1.99676600	-0.04536700	-7.11155000
H	-3.38839700	-4.67511300	-0.26221300	H	0.85429000	0.98024600	-6.86096700
H	-1.71301400	-5.19161100	-0.05046900	H	-0.13321800	-1.32980500	-7.32710700
H	-2.08814500	-3.50932300	-0.47790700	H	-1.34396600	-2.31216000	-7.55649200
C	2.59200200	-1.83298100	2.58589200	H	0.02616700	2.01766400	1.58251300
C	2.92811000	-3.17430400	2.24727500	H	0.19576100	3.44127200	2.18204300
C	4.26976400	-3.52630500	2.08756000	H	-0.85429000	-0.98024600	6.86096700
H	4.52289800	-4.55072100	1.83029100	H	-1.99676600	0.04536700	7.11155000
C	5.28952200	-2.59598600	2.23888600	H	1.34396600	2.31216000	7.55649200
H	6.32683100	-2.88935700	2.10935800	H	0.13321800	1.32980500	7.32710700

Table S11. Cartesian coordinates of the optimized geometry for **4'**.

Mg	-5.01299400	0.34086900	1.32193800	N	-5.12069900	-1.12036400	-0.10941100
K	1.50165000	0.37486500	1.72328400	N	-3.20804100	0.12174200	2.39639700
O	-5.70540100	2.08806200	2.28701000	N	-2.18392400	-0.03414400	1.82787200
O	-6.23215900	-0.84797600	2.55777500	N	-1.17015600	-0.18257000	1.26623600
O	0.52371300	2.00686200	3.60033700	C	-4.51151200	0.77881900	-1.45955800
N	-4.81607100	1.52679200	-0.34584500	C	-4.68820600	-0.66265900	-1.33203100

C	-4.41739100	-1.46409200	-2.45299800	C	3.79861400	-0.45055100	3.79042800
H	-4.56489000	-2.53888000	-2.36580300	H	3.46623700	-0.89639500	4.72767100
C	-3.98221000	-0.92009500	-3.67477700	C	4.05848300	-1.28619900	2.68781000
H	-3.78135200	-1.58607800	-4.51284400	H	3.95095200	-2.36398600	2.79743500
C	-3.79863300	0.45046800	-3.79045300	C	4.73889200	-2.92309900	0.37095900
H	-3.46622800	0.89628100	-4.72770300	C	5.90437900	-3.70849300	0.48689400
C	-4.05845600	1.28616000	-2.68786200	C	5.86391400	-5.09575300	0.34527100
H	-3.95089700	2.36394100	-2.79749200	H	6.78506400	-5.67327400	0.43401500
C	-4.73873800	2.92313400	-0.37103600	C	4.65564700	-5.74481400	0.09969300
C	-5.90416100	3.70861000	-0.48710600	H	4.62454000	-6.82836600	-0.01500700
C	-5.86360000	5.09587000	-0.34554400	C	3.48562100	-4.99134000	0.00579700
H	-6.78468800	5.67347000	-0.43436000	H	2.53206300	-5.48779400	-0.18096700
C	-4.65530300	5.74484700	-0.09986500	C	3.52582400	-3.60612400	0.13991800
H	-4.62415800	6.82839400	0.01484900	C	5.36651200	2.47811500	-0.11133000
C	-3.48534800	4.99128800	-0.00580600	C	4.34558900	3.37368300	-0.48694900
H	-2.53178000	5.48768100	0.18104500	C	4.62913900	4.68935900	-0.83829500
C	-3.52564300	3.60607600	-0.13992200	H	3.81645400	5.35435600	-1.13485400
C	-5.36664700	-2.47803500	0.11140100	C	5.94380300	5.15847500	-0.83427600
C	-4.34569400	-3.37359700	0.48695000	H	6.16336800	6.18709700	-1.11971200
C	-4.62921300	-4.68925600	0.83836800	C	6.96971400	4.29470200	-0.45896600
H	-3.81652800	-5.35427100	1.13488100	H	8.00140300	4.64998400	-0.43680800
C	-5.94388400	-5.15835800	0.83449100	C	6.68573300	2.97746900	-0.09677200
H	-6.16346000	-6.18696600	1.11998200	H	6.43380100	1.69692500	-2.13531900
C	-6.96982900	-4.29459700	0.45924700	H	6.01632000	1.14538200	-3.44909200
H	-8.00152100	-4.64987300	0.43719100	H	5.69882900	-2.88253000	-1.73280500
C	-6.68587000	-2.97737700	0.09697800	H	5.59547700	-2.40876600	-3.18808000
Mg	5.01296700	-0.34077900	-1.32196800	H	-6.01655900	-1.14523200	3.44902600
K	-1.50170400	-0.37493800	-1.72331600	H	-6.43391100	-1.69675000	2.13521900
O	5.70548300	-2.08790500	-2.28706500	H	-5.59541100	2.40893300	3.18802400
O	6.23199800	0.84815300	-2.55785200	H	-5.69867100	2.88267800	1.73273700
O	-0.52380200	-2.00742300	-3.59998000	H	0.66607100	1.91544100	4.55125600
N	4.81611100	-1.52675200	0.34579700	H	-0.00478100	2.81176900	3.52083600
N	5.12055900	1.12043800	0.10942000	H	0.00467300	-2.81232200	-3.52027200
N	3.20803700	-0.12180000	-2.39643800	H	-0.66611200	-1.91621500	-4.55092700
N	2.18388300	0.03400600	-1.82795800	H	-2.61784600	3.01591800	-0.05056900
N	1.17011300	0.18247100	-1.26633700	H	-6.83976700	3.19604500	-0.69181400
C	4.51151500	-0.77881600	1.45952700	H	-3.32709200	-2.99818600	0.53436500
C	4.68809800	0.66266600	1.33203400	H	-7.47542900	-2.30935100	-0.23976700
C	4.41729900	1.46409400	2.45303400	H	2.61798200	-3.01603000	0.05061500
H	4.56475700	2.53888600	2.36582400	H	6.83996500	-3.19586900	0.69154900
C	3.98216000	0.92002500	3.67479700	H	3.32699300	2.99827300	-0.53447000
H	3.78128000	1.58598300	4.51288000	H	7.47526900	2.30943300	0.23999900

Table S12. Cartesian coordinates of the optimized geometry for **5'**

Mg	-2.72933400	-0.03751900	0.11549400	H	0.39863200	2.07097900	-2.80045300
O	1.14777800	0.31849400	-1.31521900	C	-2.82435800	0.81196700	-3.00934600
N	-4.27132400	1.25390300	0.51073500	H	-3.32639400	-0.13991200	-2.81453300
N	-4.24382700	-1.39564900	-0.14466900	H	-2.99592500	1.07749700	-4.05768300
N	-1.17783100	0.33573500	-1.28908600	H	-3.30160600	1.57488000	-2.38821200
C	-5.50263900	0.62070100	0.35669700	N	1.17783400	-0.33569500	1.28909200
C	-5.48797000	-0.78431700	0.00791200	C	-0.00789800	-0.18968500	0.75199800
C	-6.72230000	-1.41260000	-0.23222700	C	1.31782400	-0.72078600	2.71690600
H	-6.71951900	-2.43777000	-0.58518800	C	0.69258900	0.34631600	3.63674300
C	-7.94582600	-0.76547300	-0.04315100	H	-0.37769200	0.43738800	3.45684800
H	-8.87359600	-1.29820100	-0.24209100	H	0.84877700	0.07996900	4.68817300
C	-7.95967900	0.55051600	0.40203200	H	1.15958400	1.32069200	3.46462700
H	-8.89875800	1.06413100	0.59834700	C	0.67549900	-2.09724500	2.97689200
C	-6.75073200	1.22341200	0.59402200	H	1.11588600	-2.85151300	2.31964500
H	-6.77111400	2.24687300	0.95100400	H	0.85205700	-2.40693400	4.01323200
C	-4.11821100	2.62786100	0.50492900	H	-0.39876000	-2.07078500	2.80046500
C	-3.01442100	3.18385900	1.20194900	C	2.82435800	-0.81209000	3.00931100
C	-2.73396800	4.54325800	1.17658200	H	3.32648300	0.13974000	2.81448800
H	-1.87222200	4.91516800	1.72580400	H	2.99592400	-1.07764100	4.05764300
C	-3.54303800	5.43017400	0.46256600	H	3.30151500	-1.57504800	2.38816400
H	-3.32483100	6.49421600	0.44497100	O	-1.14777500	-0.31846600	1.31522200
C	-4.63083800	4.90808600	-0.23871900	Mg	2.72933700	0.03753600	-0.11549300
H	-5.26513700	5.57194800	-0.82393200	N	4.27130900	-1.25390100	-0.51075000
C	-4.91861700	3.54774700	-0.22310400	N	4.24384800	1.39564700	0.14467900
C	-4.06297700	-2.76468000	-0.08101000	C	5.50263300	-0.62071800	-0.35669800
C	-4.86044700	-3.67177000	0.66615000	C	5.48798400	0.78429600	-0.00789700
C	-4.55261700	-5.02563100	0.73409000	C	6.72232400	1.41254800	0.23227400
H	-5.18697700	-5.67791200	1.33232600	H	6.71956000	2.43771000	0.58525800
C	-3.44520900	-5.55586500	0.07018200	C	7.94584000	0.76540000	0.04320500
H	-3.21167100	-6.61524000	0.12851000	H	8.87361700	1.29810600	0.24217100
C	-2.63676500	-4.68126700	-0.65899300	C	7.95967400	-0.55058100	-0.40200000
H	-1.75699600	-5.05647900	-1.17642600	H	8.89874600	-1.06421200	-0.59830800
C	-2.93811100	-3.32863600	-0.73710000	C	6.75071700	-1.22345000	-0.59401500
C	0.00790200	0.18973000	-0.75199000	H	6.77108400	-2.24690800	-0.95100700
C	-1.31782300	0.72081300	-2.71690400	C	4.11818100	-2.62785600	-0.50496300
C	-0.69246100	-0.34623700	-3.63671400	C	3.01438400	-3.18383400	-1.20198900
H	0.37782400	-0.43720700	-3.45678400	C	2.73392000	-4.54323100	-1.17664000
H	-0.84864100	-0.07991200	-4.68815000	H	1.87216900	-4.91512600	-1.72586600
H	-1.15936900	-1.32065600	-3.46460400	C	3.54298400	-5.43016400	-0.46264000
C	-0.67562700	2.09733300	-2.97688900	H	3.32476700	-6.49420500	-0.44505900
H	-1.11609400	2.85156100	-2.31964900	C	4.63079100	-4.90809700	0.23864900
H	-0.85220700	2.40700200	-4.01323200	H	5.26508700	-5.57197200	0.82385000

C	4.91858200	-3.54776000	0.22305300	C	2.93816200	3.32864000	0.73714600
C	4.06301000	2.76468000	0.08102800	H	-2.29694900	-2.66784400	-1.31409800
C	4.86046000	3.67176800	-0.66615400	H	-5.70763000	-3.29219900	1.22406300
C	4.55263400	5.02563000	-0.73408500	H	-5.75179200	3.17479800	-0.80624200
H	5.18697700	5.67791000	-1.33234000	H	-2.38079400	2.51046000	1.77255100
C	3.44524700	5.55586900	-0.07014400	H	5.70762200	3.29219600	-1.22409800
H	3.21171100	6.61524500	-0.12846300	H	2.29701100	2.66784900	1.31415800
C	2.63681900	4.68127200	0.65905100	H	2.38076300	-2.51042100	-1.77258000
H	1.75706600	5.05648700	1.17650900	H	5.75176400	-3.17482600	0.80619200

References:

S1. M. Schlosser, J. Hartmann, *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 508-509; *Angew. Chem.* 1973**, 85**, 544-545.

S2. T. Wenderski, K. M. Light, D. Ogrin, S. G. Bott, C. J. Harlan, *Tetrahedron Let.* 2004, **45**, 6851-6853.

S3. V. K. Cherkasov, N. O. Druzhkov, T. N. Kocherova, A. S. Shavyrin, G. K. Fukin, *Tetrahedron* 2012, **68**, 1422-1426.

S4. G. M. Sheldrick, Program SADABS: Area-Detector Absorption Correction, **1996**, University of Göttingen, Germany.

S5. G. M Sheldrick, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun*. 2015, **71**, 3-8.

S6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Jr. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. Zakrzewski, G. S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford CT*, 2004.

S7. A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652.

S8. a) K. B. Wiberg, *Tetrahedron* 1968, **24**, 1083-1096; b) A. E. Reed, L.A. Curtiss, F. Weinhold, *Chem. Rev.* 1988, **88**, 899-926.

S9. M. Cossi, V. Barone. *J. Chem. Phys.*, 2001, **115**, 4708-4717.

S10. T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.* 2004, **393**, 51-57.

S11. Y. Liu, S. Li, X.-J. Yang, P. Yang, B. Wu, *J. Am. Chem. Soc*. 2009, **131**, 4210-4211.