Literature Report

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Communication

Full Visible Spectrum and White Light Emission with a Single, Input-Tunable Organic Fluorophore

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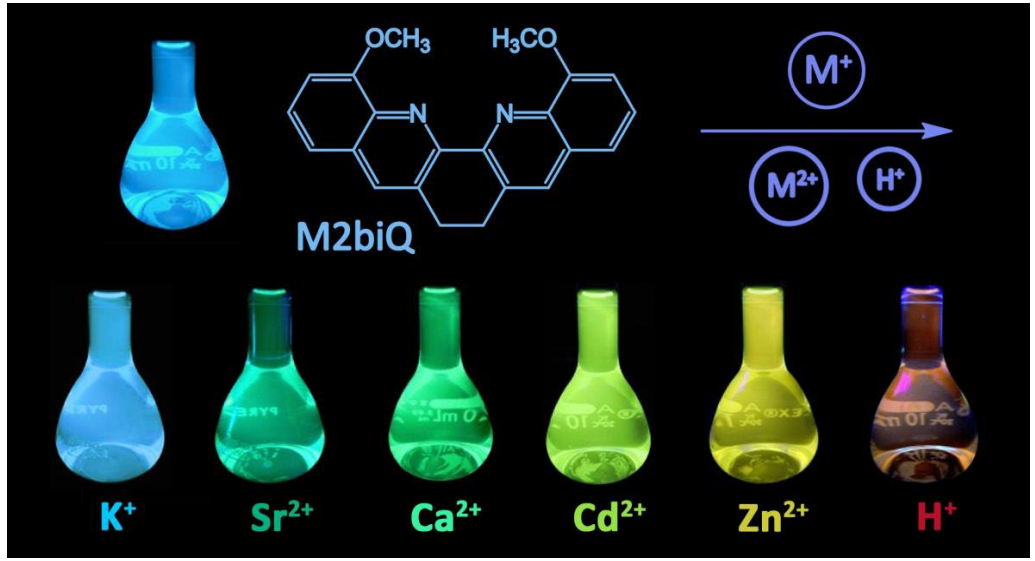
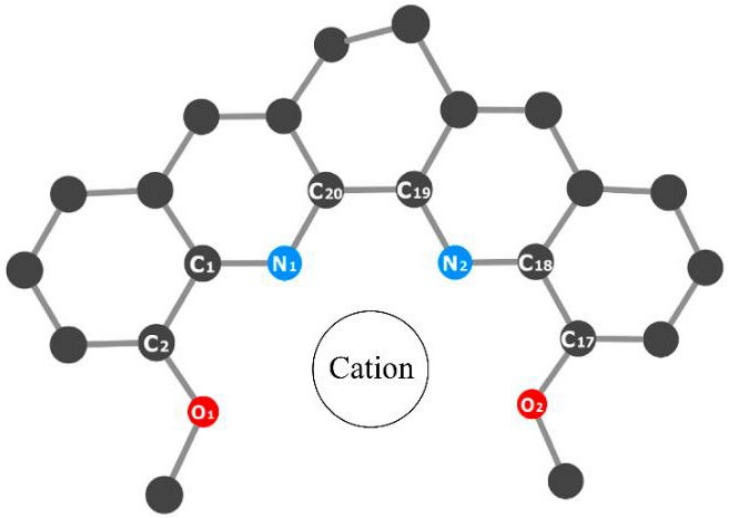
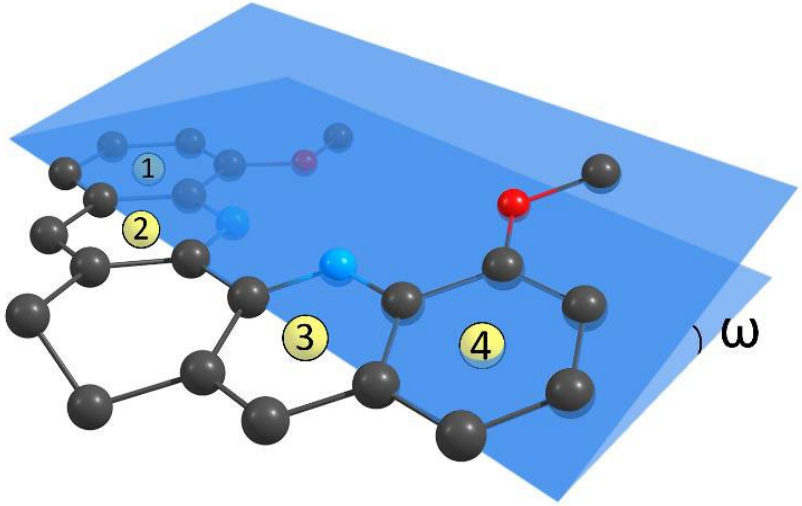
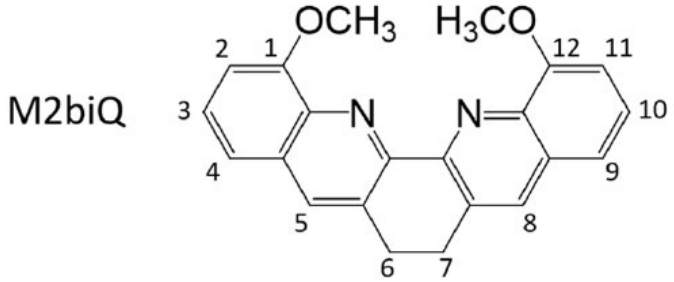


探针设计





离子调控



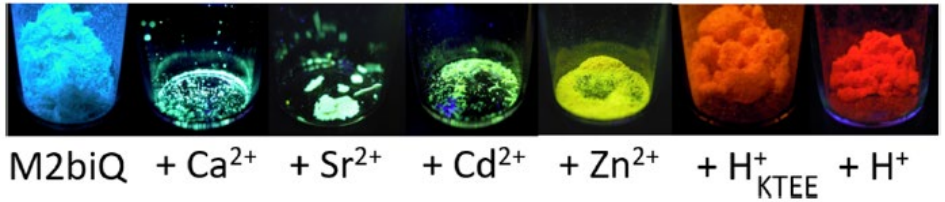
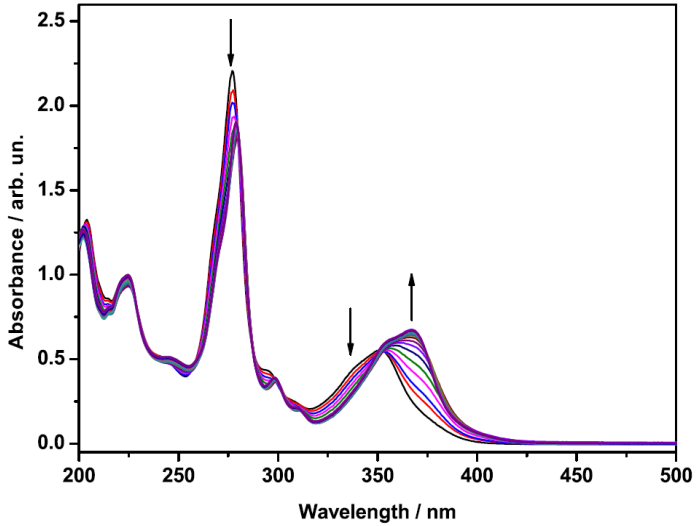
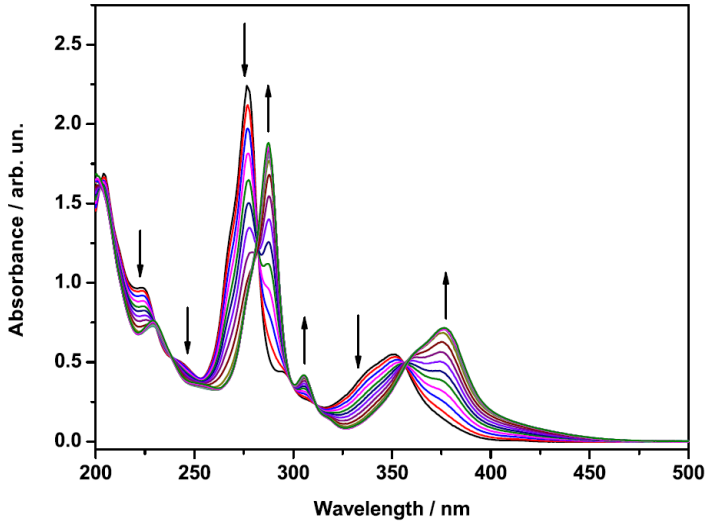
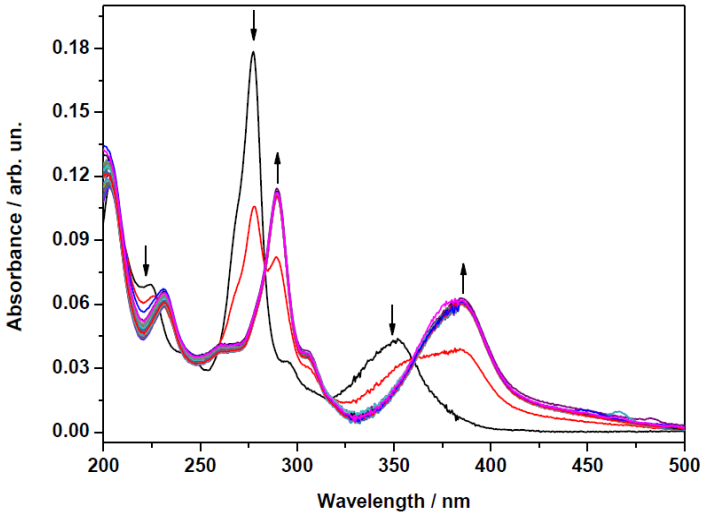


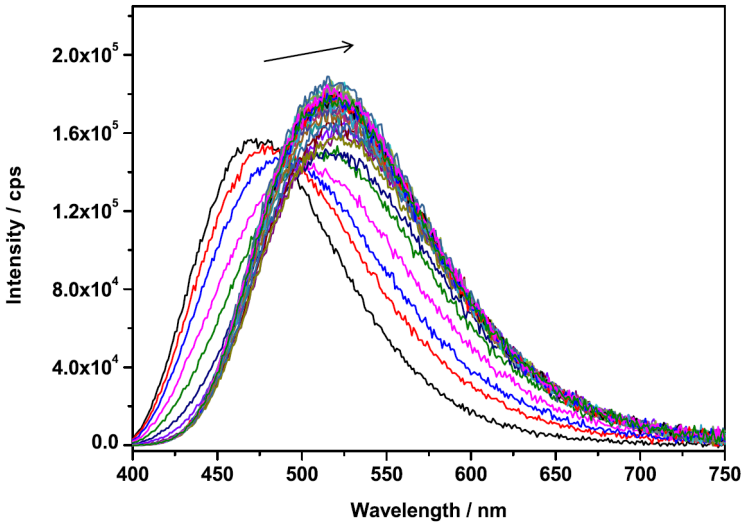
Figure 1. Structure of M2biQ and solid-state fluorescence (λ_{ex} = 365 nm) of the free ligand and some of its salts. All samples were isolated from wet acetonitrile except for H^{+}_{KTEE}, which was isolated from KOH/TFA/EtOH/Ether (KTEE). All other counterions are ClO_4^-. See pp S66, 72 for details.

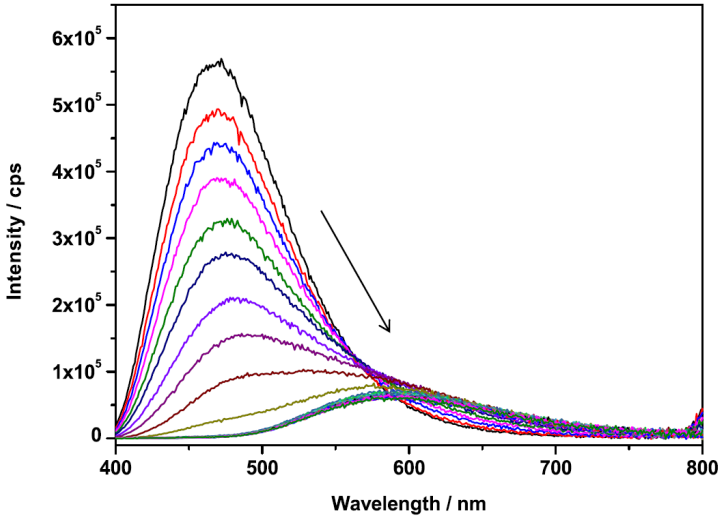
探针离子滴定

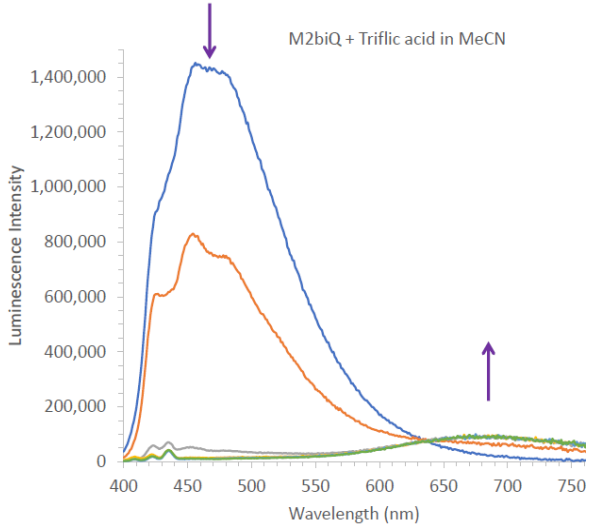












Ca^{2+}

Zn^{2+}

H^{+}

探针光谱性质

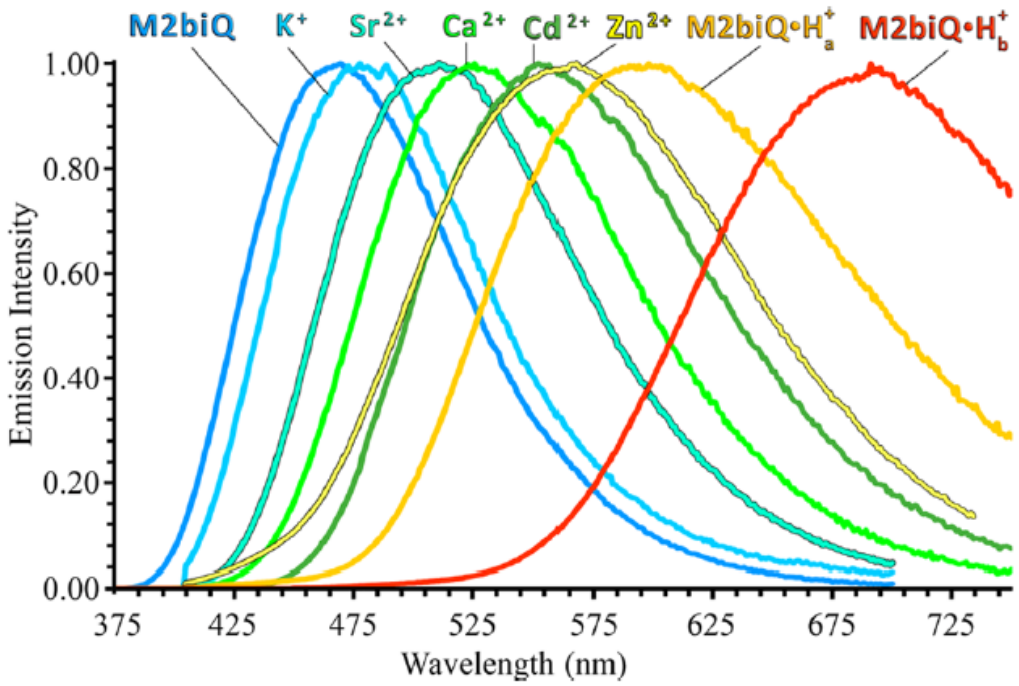


Figure 2. Normalized emission spectra of M2biQ and its complexes (10^{-4} M) in MeCN. Salts used: KSCN, $Sr(ClO_4)_2$, $Ca(ClO_4)_2$, $Cd(NO_3)_2$, and $Zn(ClO_4)_2$. H_a^+ = TFA/MeCN (1:4, v/v) and H_b^+ = HCl (generated *in situ*). See pp S32–S33, for details.

Table 2. Experimental and Calculated (c) Absorption and Emission Wavelengths (λ_{max}, nm) of M2biQ Species in Acetonitrile ([M2biQ] = 10^{-4} M)

Species[a]	λ_{abs}	λ_{abs} (c)	λ_{abs}	λ_{abs} (c)	λ_{em}	λ_{em} (c)
M2biQ	276	294	352	331	468	456
M2biQ·K^+	276	290	356	342	477	458
M2biQ·Sr^{2+}	273	287	366	353	510	485
M2biQ·Ca^{2+}	279	288	367	359	528	489
M2biQ·Cd^{2+}	282	293	368	362	551	514
$M2biQ_2$·Zn^{2+}	288	303	376	369	581	558
M2biQ·H^+	290	304	384	380	690	585

Table 3. Quantum Yields and Lifetimes for RGB and Yellow Emitters in Acetonitrile[a]

Substance	Quantum yield, φ	Reference Standard	Lifetime τ (/ns)
M2biQ	0.25	Quinine sulfate[69,70]	5.55 ± 0.03
M2biQ·Ca^{2+}	0.44	Fluorescein[70,71]	17.3 ± 0.01
$M2biQ_2$·Zn^{2+}	0.01	$Ru(bpy)_3Cl_2$[70,71]	6.88 ± 0.03
M2biQ·H^+	0.001	$Ru(bpy)_3Cl_2$[70,71]	Unable to measure

晶体结构表征

M2biQ·H_2O·$CHCl_3$ M2biQ·$Ca(ClO_4)_2$ M2biQ·$Zn(ClO_4)_2$·$2H_2O$ M2biQ·$HClO_4$·H_2O

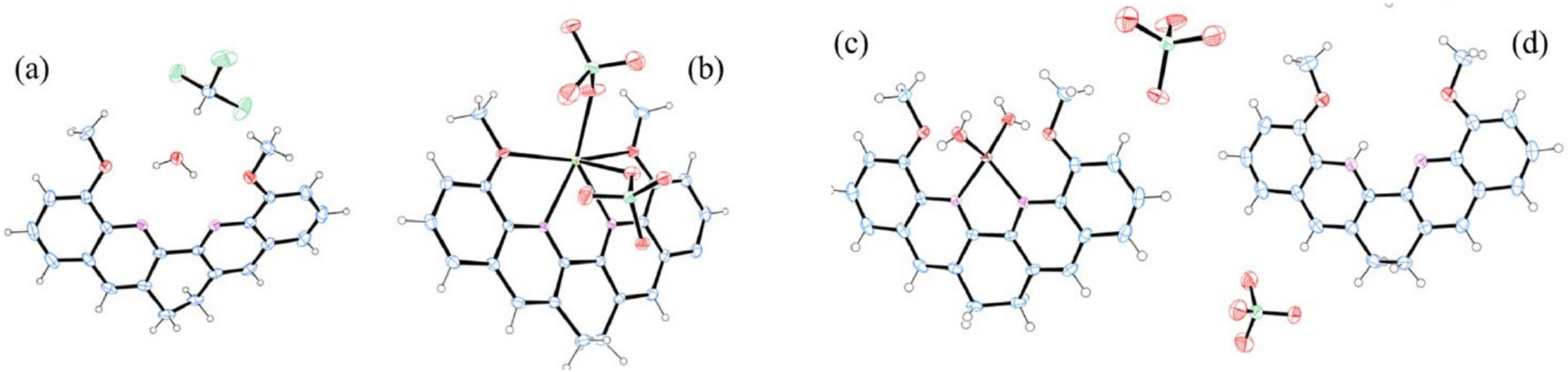


Table 1. Bond Lengths[a] and Dihedral Angles NC–CN and ω in Single Crystal X-ray Structures Corresponding to RGB and Yellow Species

Crystal	Bond Length/Å N–Guest	Bond Length (Å) O–Guest	Dihedral angle NC–CN (ω)[b]
M2biQ·H_2O	2.46/2.53 (N---H_2O)	2.15/2.20 (O---H_2O)	23.8° (24.3°)
M2biQ·Ca^{2+}	2.46/2.47 (N–Ca^{2+})	2.50/2.51 (O–Ca^{2+})	9.0° (10.4°)
M2biQ·Zn^{2+}	2.05/2.05 (N–Zn^{2+})	2.62/2.62 (O–Zn^{2+})	8.1° (10.2°)
M2biQ·H^+	0.86 (N–H^+)	2.31 (O---H^+)	7.5° (7.9°)
M2biQ$_2$·Zn^{2+}	2.04/2.04 (N–Zn^{2+})	2.71/2.71 (O–Zn^{2+})	7.1° (11.2°)
(pair 1)	2.06/2.06 (N–Zn^{2+})	2.74/2.74 (O–Zn^{2+})	14.0° (12.6°)
M2biQ$_2$·Zn^{2+}	2.06/2.06 (N–Zn^{2+})	2.76/2.77 (O–Zn^{2+})	16.5° (19.6°)
(pair 2)	2.04/2.04 (N–Zn^{2+})	2.67/2.78 (O–Zn^{2+})	16.0° (18.8°)

晶体结构表征

1:1配位

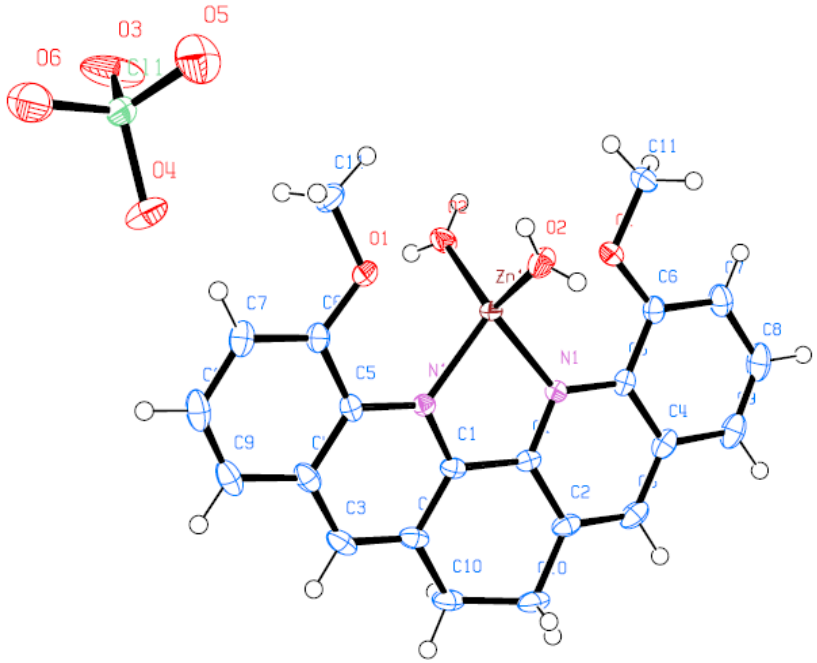


Figure S140. Crystal structure of M2biQ·Zn(ClO_4)$_2$. C atoms (blue), O atoms (red), N atoms (violet), Cl atoms (green), H atoms (white), Zn ion (brown).

1:2配位

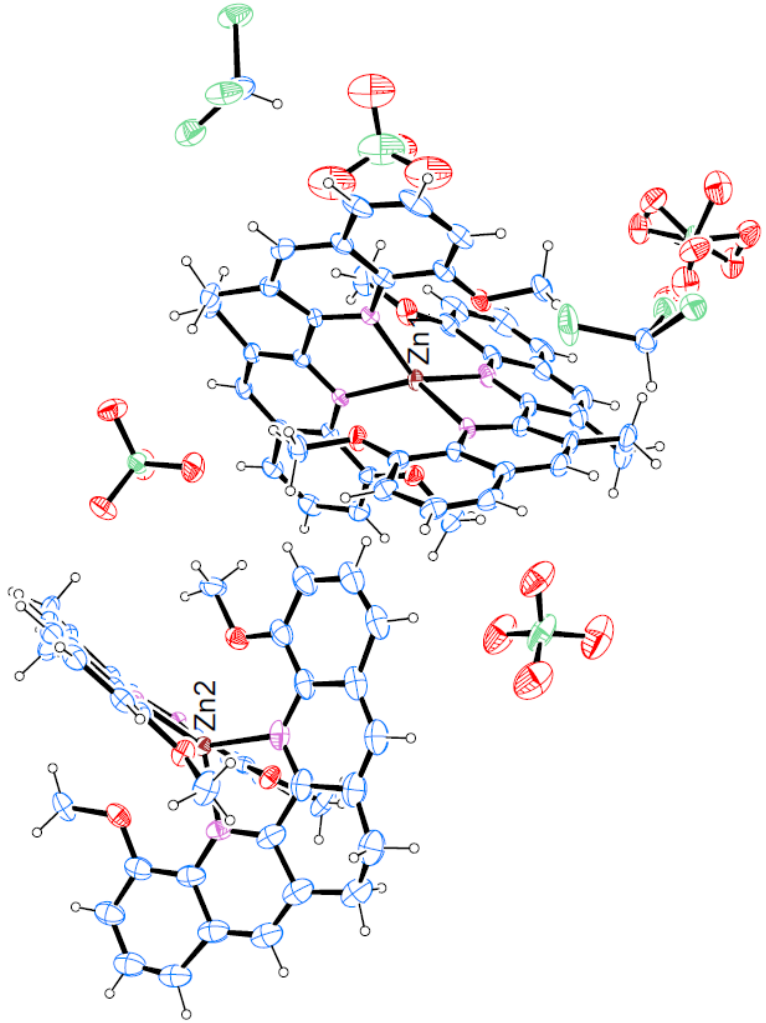


Figure S142. Another view of the crystal structure of M2biQ$_2$·Zn(ClO_4)$_2$. C atoms (grey), O atoms (red), N atoms (blue), Cl atoms (green), Zn ions (violet).

理论计算

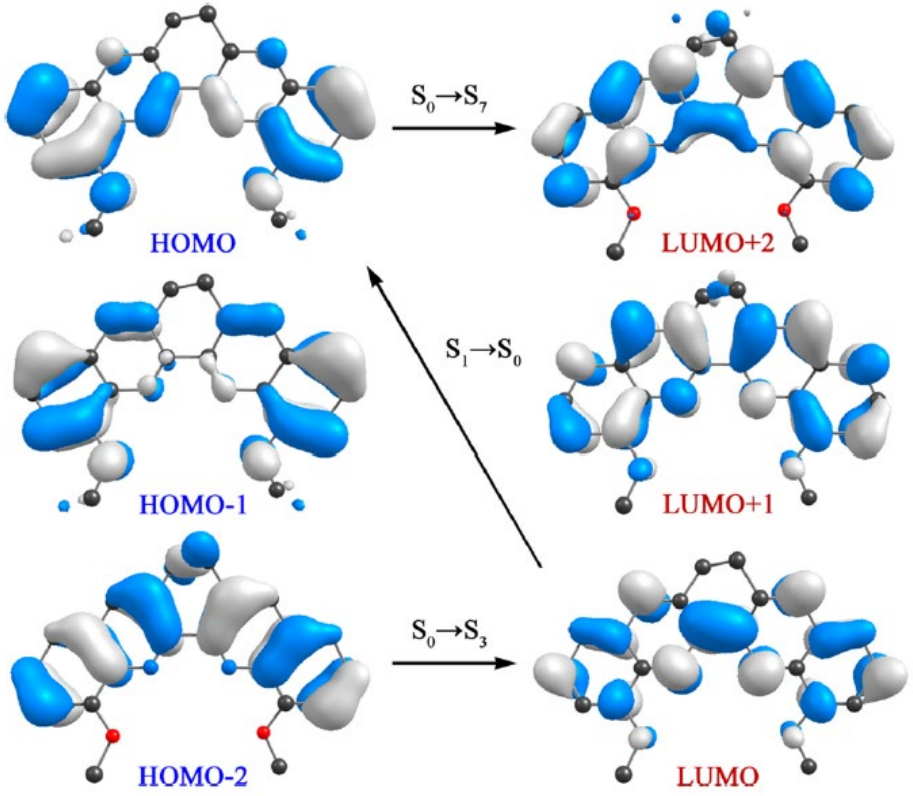
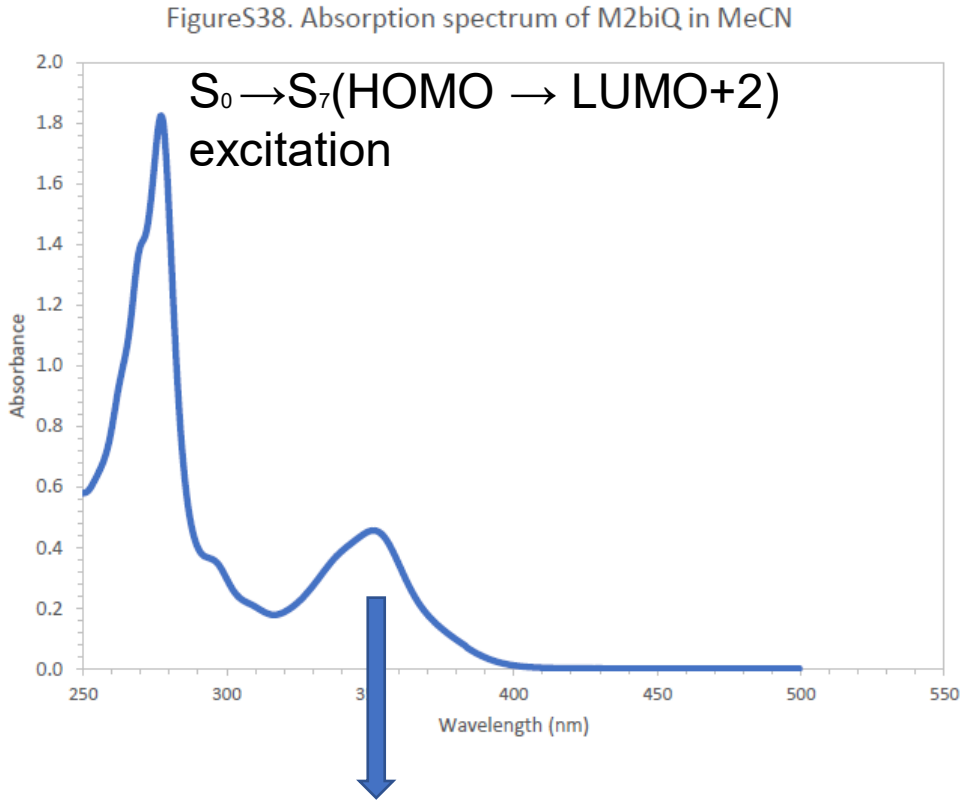


Figure 4. M2biQ frontier molecular orbitals at the equilibrium geometry of the ground state.



excitations $S_0 \rightarrow S_1$(HOMO → LUMO), $S_0 \rightarrow S_2$ (HOMO−1 → LUMO), and $S_0 \rightarrow S_3$ (HOMO−2 → LUMO)

理论计算

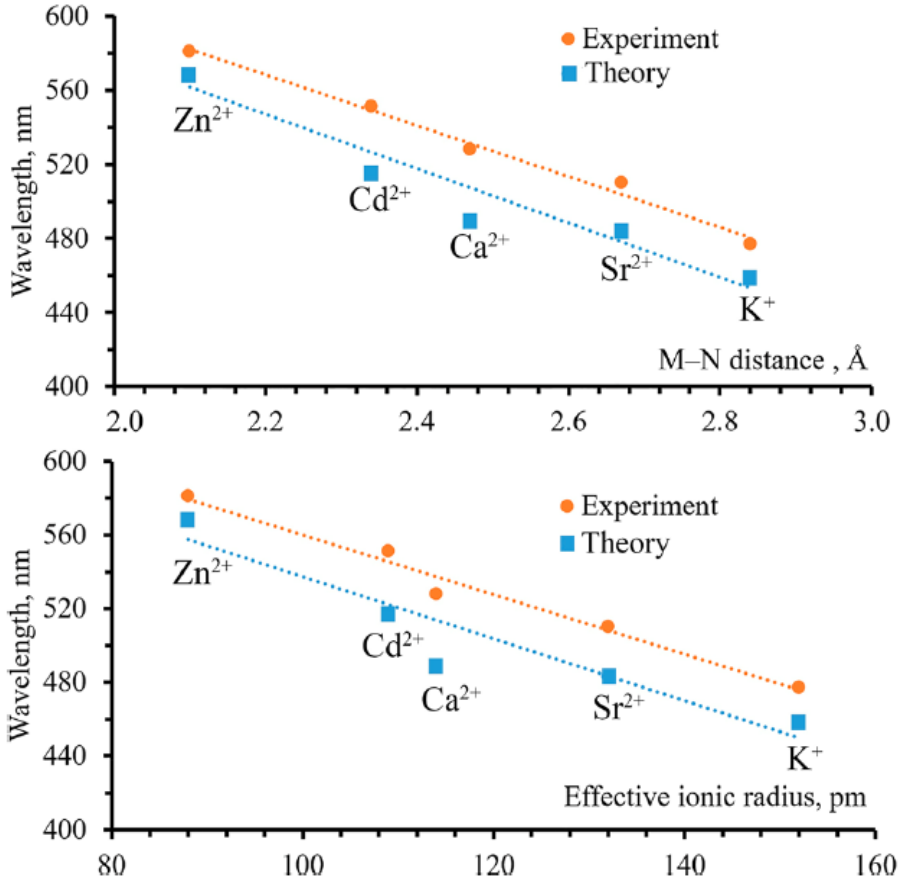


Figure 5. Correlations of ionic radii and metal−nitrogen distances with experimentally measured and computed emission wavelengths in 1:1 M2biQ complexes.

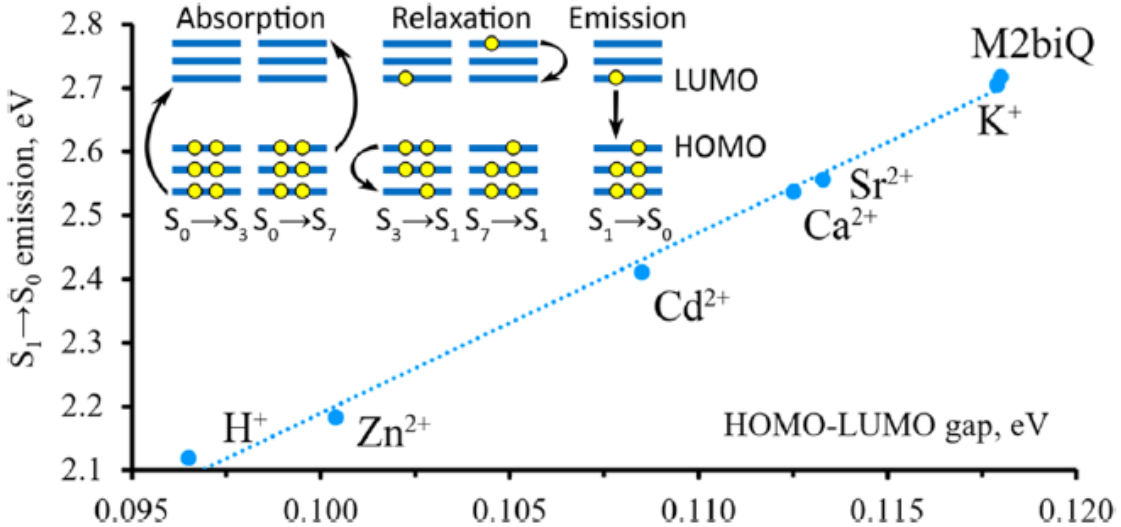


Figure 6. Proposed mechanism for M2biQ absorption and emission (inset) and correlation between calculated HOMO−LUMO gaps and energy differences between S_1 and S_0 states at the S_1 minimum.