Supporting Information

Photophysical Heavy-Atom Effect in Iodinated Metallocorroles: Spin-orbit Coupling and Density of States

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FIGURES

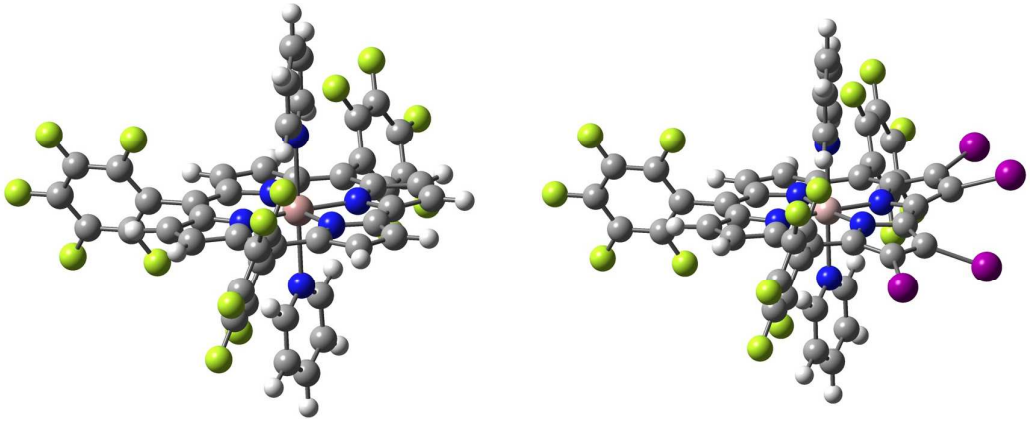

Figure S1. DFT-optimized structures of **0-Ga** (left) and **4-Ga** (right) in toluene described by a polarizable continuum model. The I atoms deviate from the ligand plane by ca. 16.5° (calculated as a half of the I-C-C-I angle). I atoms lie ca. 1 Å above or below the ligand plane. Very similar structures were obtained for **4-Al**. Iodine atoms do not deviate from planarity in the optimized structure of **3-Ga**.

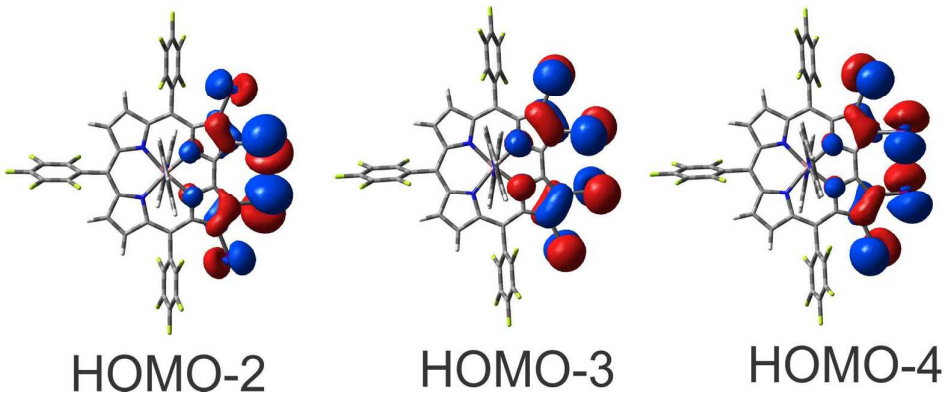

Figure S2. Shapes of the HOMO-2,3,4 of **4-Ga**.

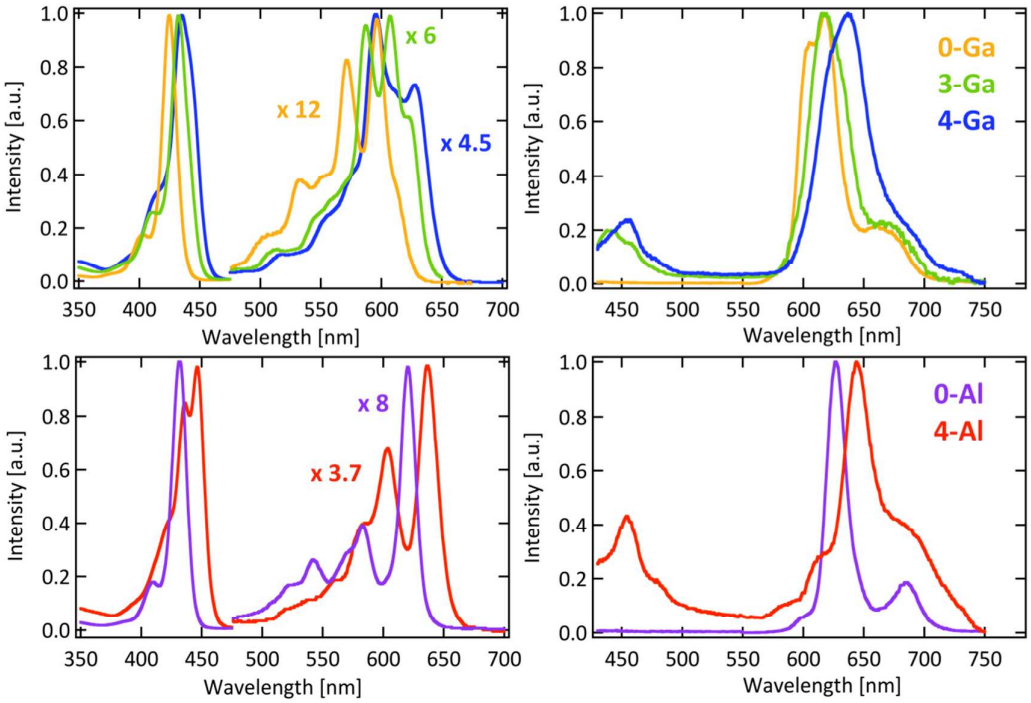

Figure S3. Comparison of normalized steady-state absorption (left) and emission spectra (right) obtained upon 400 nm excitation.

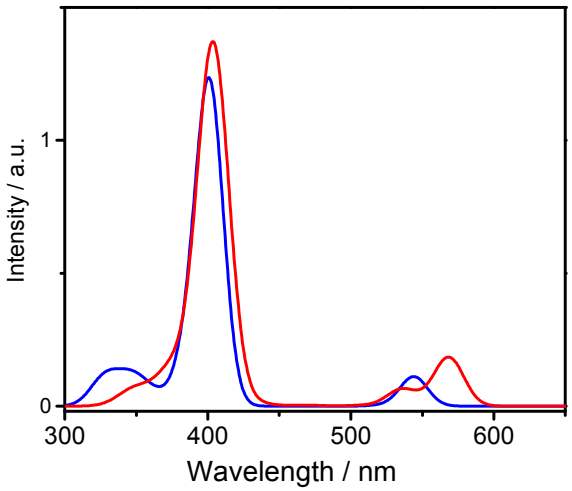

Figure S4. Simulated absorption spectra of **0-Ga** (blue) and **4-Ga** (red) in toluene (SO-TDDFT/ADF/B3LYP/COSMO-Toluene). 1500 cm^{-1} FWHM assumed.

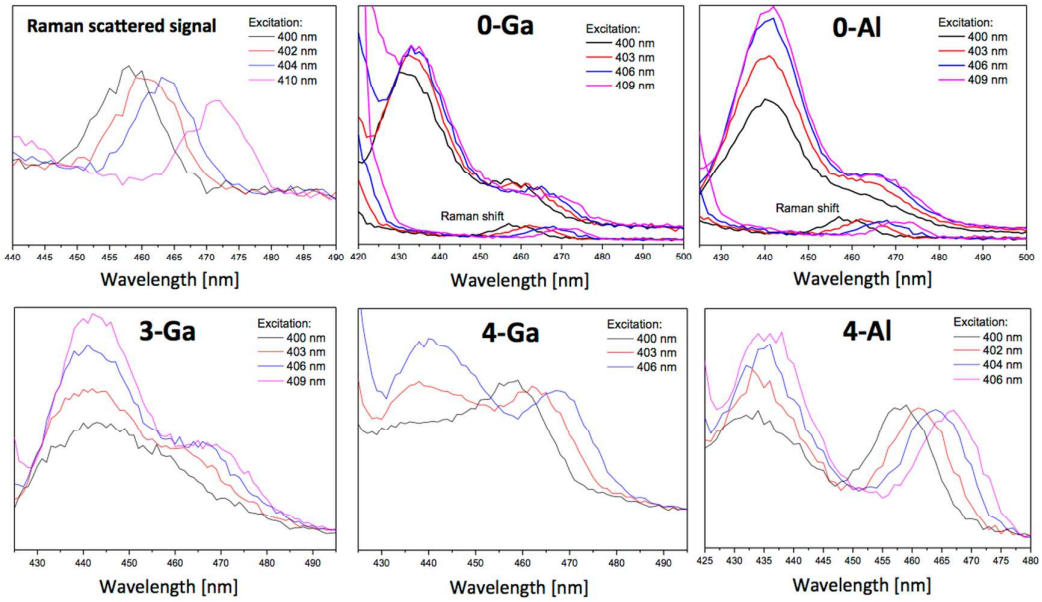

Figure S5. Steady-state emission spectra of all investigated corrole complexes in the region of the Soret emission as a function of the excitation wavelength. Top-left: pure Raman signal. All measurements in toluene / 5% pyridine except **4-Al** (pure toluene).

Distinguishing Soret emission from solvent Raman scattering: In order to prove the Soret origin of the 420-480 nm spectral feature and distinguish it from the solvent Raman band, emission spectra were measured at several excitation wavelengths in the blue side of the Soret absorption (Figure S5). Whereas the fluorescence band does not shift with the excitation wavelength and its intensity increases as the excitation wavelength moves deeper into the Soret absorption band, the Raman peak maximum shifts with the excitation wavelength and its intensity stays approximately constant.

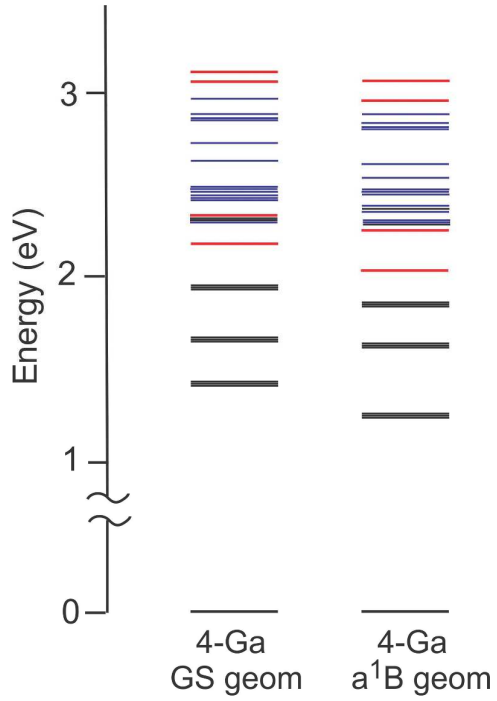

Figure S6. Electronic state diagram of **4-Ga** calculated at the ground-state (left) and lowest-singlet (right) optimized geometries. (SO-TDDFT/ADF/B3LYP/COSMO-Toluene)

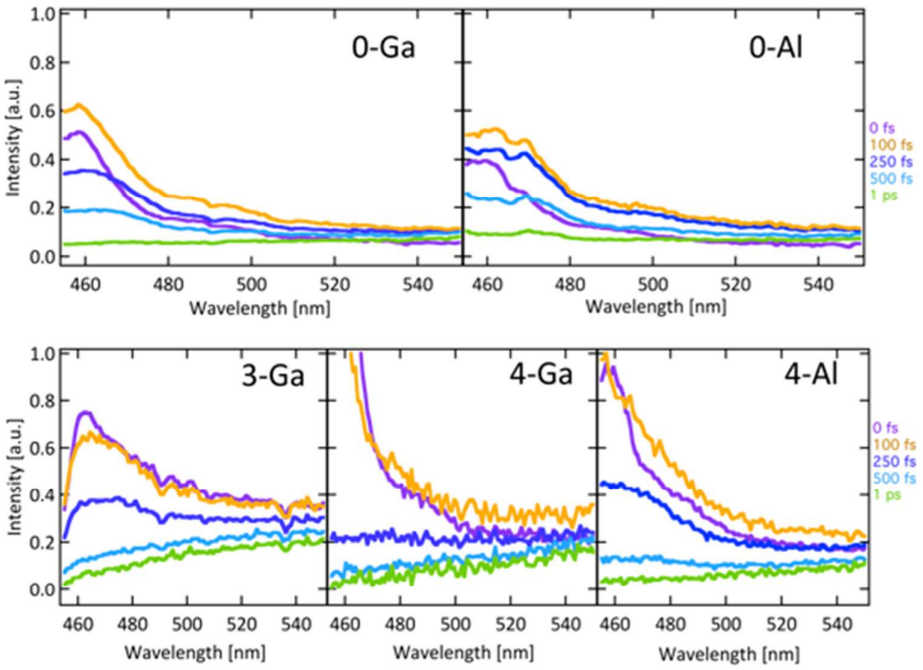

Figure S7. Selected time-resolved fluorescence spectra in the Soret region.

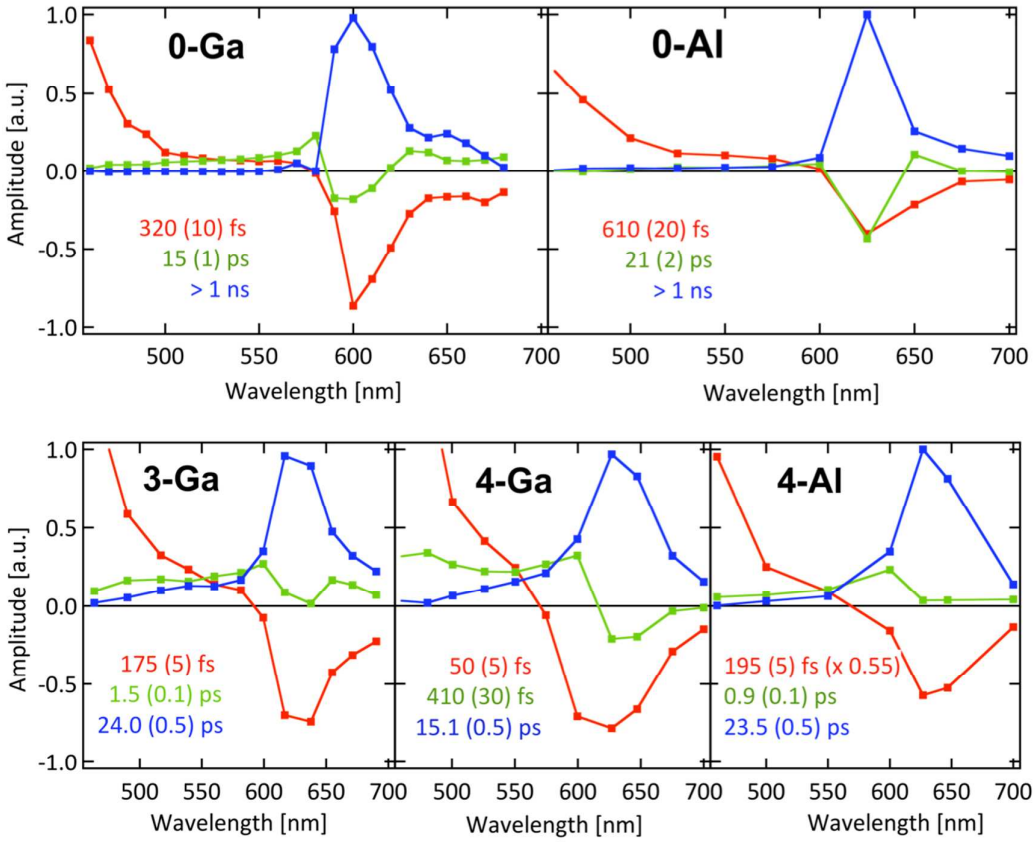

Figure S8. Results of global triexponential fitting of 10-15 fluorescence kinetics traces for each complex. Lifetimes are specified in the insets. The plots show dependences of the corresponding preexponential factors on the emission wavelength. Global fitting results closely match the SVD analysis presented in the main text (Figure 5, Table 1).

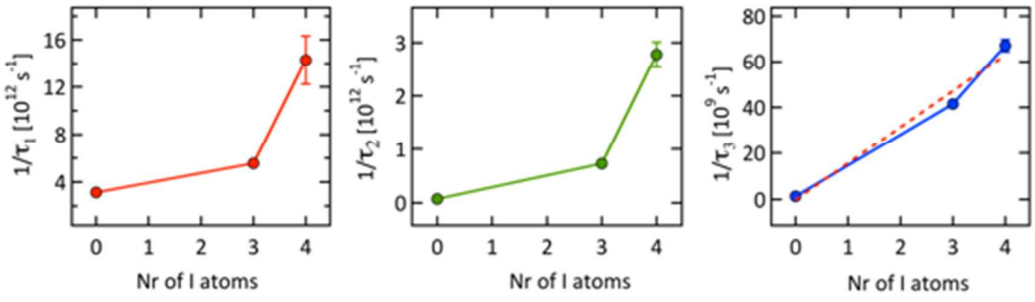

Figure S9. Photophysical rate constants ($1/\tau_i$) as a function of the number of I atoms in the Ga-based corroles. Left: Soret fluorescence decay, middle: Q vibrational relaxation, right: Q lifetime fitted with the red dashed line. (Data from Table 1.)

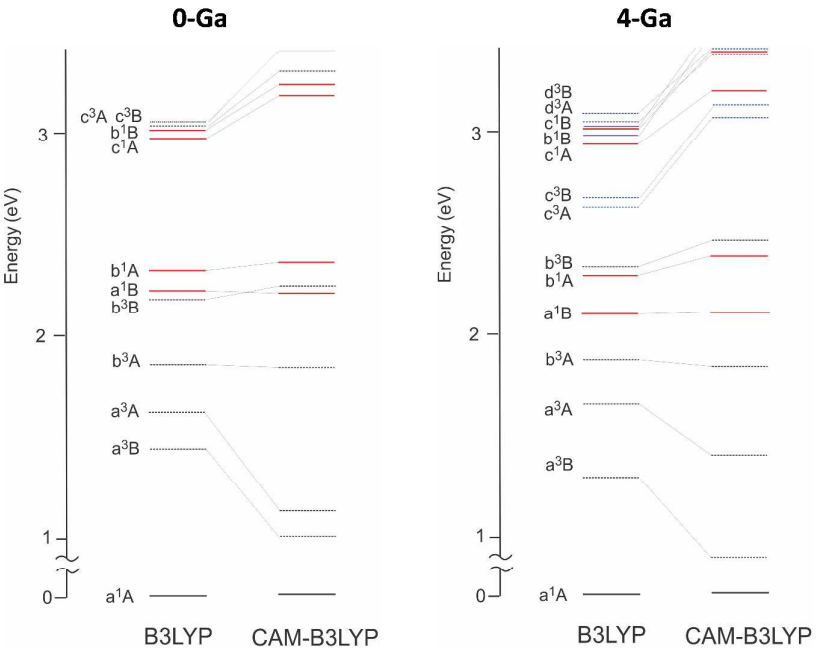

Figure S10. Excited-state correlation diagrams of **0-Ga** (left) and **4-Ga** (right) calculated by TDDFT/G16/B3LYP/PCM-toluene and TDDFT/G16/CAM-B3LYP/PCM-toluene. Red lines correspond to singlet Q and Soret excitations, blue lines indicate states with CT contributions; dashed lines correspond to triplet states.

TABLES

Table S1. DFT (B3LYP/COSMO-Toluene) calculated one-electron energies and compositions of selected frontier molecular orbitals of the investigated Ga corrole complexes.

	0-Ga			**3-Ga**			**4-Ga**		
MO	E (eV)	%I	%Ga	E (eV)	%I	%Ga	E (eV)	%I	%Ga
Unoccupied									
LUMO+3	-1.76	-	0.30	-1.87	0	0.35	-1.87	0	0.55
LUMO+2	-1.76	-	0.78	-1.85	0	1.18	-1.88	0	0.88
LUMO+1	-2.56	-	0.23	-2.68	0	0.22	-2.69	0	0.45
LUMO	-2.96	-	0.13	-3.17	2.3	0.14	-3.29	3.4	0.20
Occupied									
HOMO	-5.55	-	0.35	-5.71	3.9	0.26	-5.76	3.1	0.12
HOMO-1	-5.75	-	0.04	-5.92	7.1	0.04	-5.95	9.6	0.04
HOMO-2	-7.15	-	0.29	-6.63	55	0.27	-6.52	79	0.16
HOMO-3	-7.34	-	0.57	-6.85	48	0.44	-6.57	56	0.34
HOMO-4	-7.41	-	0.20	-6.96	52	0.19	-6.73	78	0.18

Table S2. DFT (B3LYP/COSMO-Toluene) calculated one-electron energies and compositions of selected frontier molecular orbitals of **4-Ga**.

	4-Ga					
MO	E (eV)	%I	%Ga	%N(ring)	%N(ring)	%N(py)
Unoccupied						
LUMO+3	-1.87	0	0.55	0	0	21
LUMO+2	-1.88	0	0.88	0	0	4
LUMO+1	-2.69	0	0.45	7	2	0
LUMO	-3.29	3.4	0.20	1	5	0
Occupied						
HOMO	-5.76	3.1	0.12	7	12	2
HOMO-1	-5.95	9.6	0.04	3	0	0
HOMO-2	-6.52	79	0.16	10	0	1
HOMO-3	-6.57	56	0.34	16	0	0

Table S3. DFT (B3LYP/COSMO-Toluene) calculated one-electron energies and compositions of selected frontier molecular orbitals of the investigated Al complexes.

	0-Al			**4-Al**		
MO	E (eV)	%I	%Al	E (eV)	%I	%Al
Unoccupied						
LUMO+3	-1.59	-	0.28	-1.74	0	0.55
LUMO+2	-1.60	-	1.00	-1.75	0	0.88
LUMO+1	-2.20	-	0.41	-2.40	0	0.45
LUMO	-2.59	-	0.17	-2.98	3.5	0.20
Occupied						
HOMO	-5.12	-	0.16	-5.40	2.4	0.12
HOMO-1	-5.33	-	0.08	-5.63	8.0	0.04
HOMO-2	-6.79	-	0.18	-6.37	69	0.16
HOMO-3	-6.99	-	0.49	-6.40	52	0.34
HOMO-4	-7.11	-	0.22	-6.57	70	0.21

Table S4. Lowest TDDFT-calculated spin-free electronic transitions of **0-Ga** with oscillator strengths larger than 0.005 (ADF/B3LYP/COSMO-Toluene).

State	Main components (%)	Calculated transitions (eV)[a]	Oscillator strength
a^1B	HOMO $\rightarrow$ LUMO (78) HOMO-1 $\rightarrow$ LUMO +1 (21)	2.28 (544)	0.110
b^1A	HOMO-1 $\rightarrow$ LUMO (56) HOMO $\rightarrow$ LUMO +1 (43)	2.36 (525)	0.044
b^1B	HOMO-1 $\rightarrow$ LUMO +1(71) HOMO $\rightarrow$ LUMO (17)	3.10 (400)	0.561
c^1A	HOMO $\rightarrow$ LUMO +1 (42) HOMO-1 $\rightarrow$ LUMO (32)	3.08 (402)	0.627

[a] wavelength (nm) in parenthesis

Table S5. TDDFT-calculated lowest spin-free electronic transitions of **4-Ga** (ADF/B3LYP/COSMO-Toluene).

State	Main components (%)	Calculated transitions (eV) [a]	Oscillator strength
a^3B	HOMO → LUMO (97)	1.40 (883)	-
a^3A	HOMO-1 → LUMO (91)	1.67 (743)	-
b^3A	HOMO → LUMO+1 (89)	1.94 (640)	-
a^1B	HOMO → LUMO (85) HOMO-1 → LUMO+1 (13)	2.18 (569)	0.184
b^3B	HOMO-1 → LUMO+1 (93)	2.30 (538)	-
b^1A	HOMO-1 → LUMO (68) HOMO → LUMO +1 (31)	2.32 (534)	0.065
c^3A	HOMO-3 → LUMO (94)	2.46 (504)	-
c^3B	HOMO-2 → LUMO (74)	2.50 (497)	-
b^1B	HOMO-2 → LUMO (97)	2.72 (456)	0.005
c^1A	HOMO-3 → LUMO (98)	2.78 (446)	7.10^{-4}
d^3B	HOMO-4 → LUMO (76)	2.80 (443)	-
c^1B	HOMO-4 → LUMO (92)	2.90 (427)	2.10^{-5}
d^1A	HOMO → LUMO+1 (60) HOMO-1 → LUMO (27)	3.05 (406)	0.876
d^1B	HOMO-1 → LUMO+1 (72) HOMO → LUMO (12)	3.11 (399)	0.604

[a] wavelength (nm) in parenthesis.