Supporting information

Photophysicochemical behavior of symmetric and asymmetric zinc phthalocyanines, surface assembled onto gold nanotriangles

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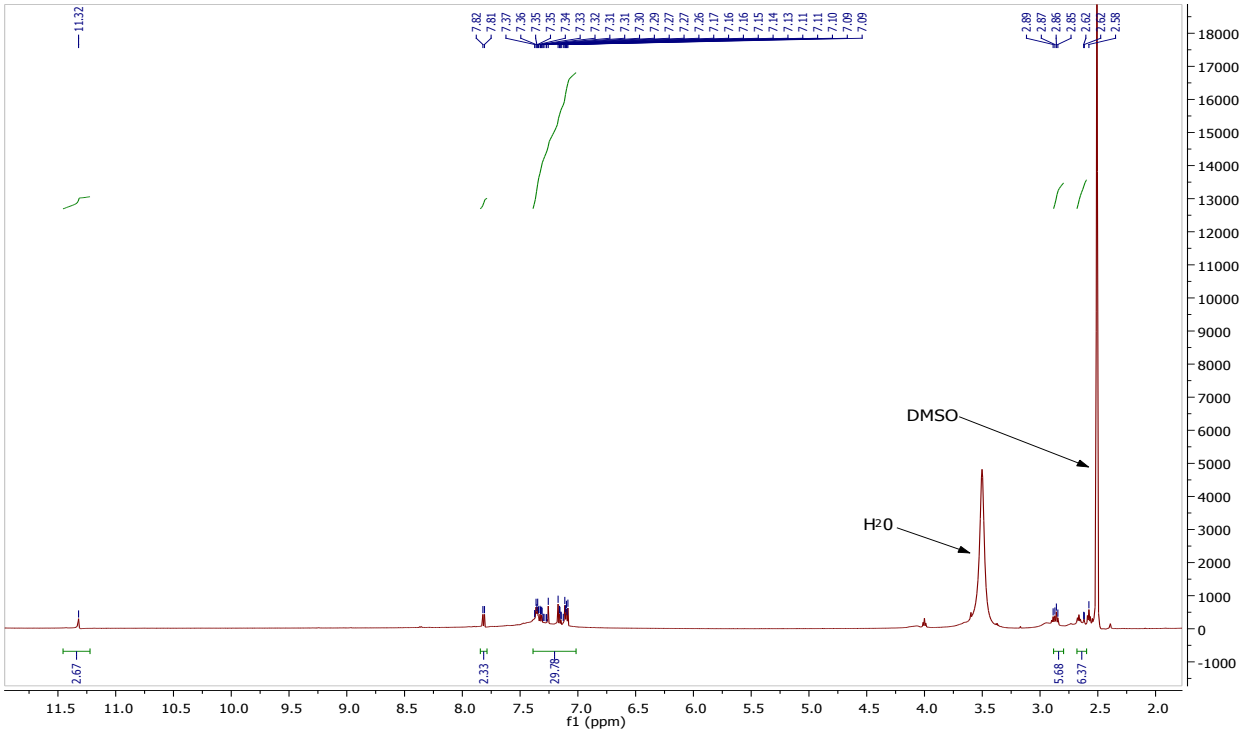


Fig. S1. ^{1}H NMR of complex **3**.

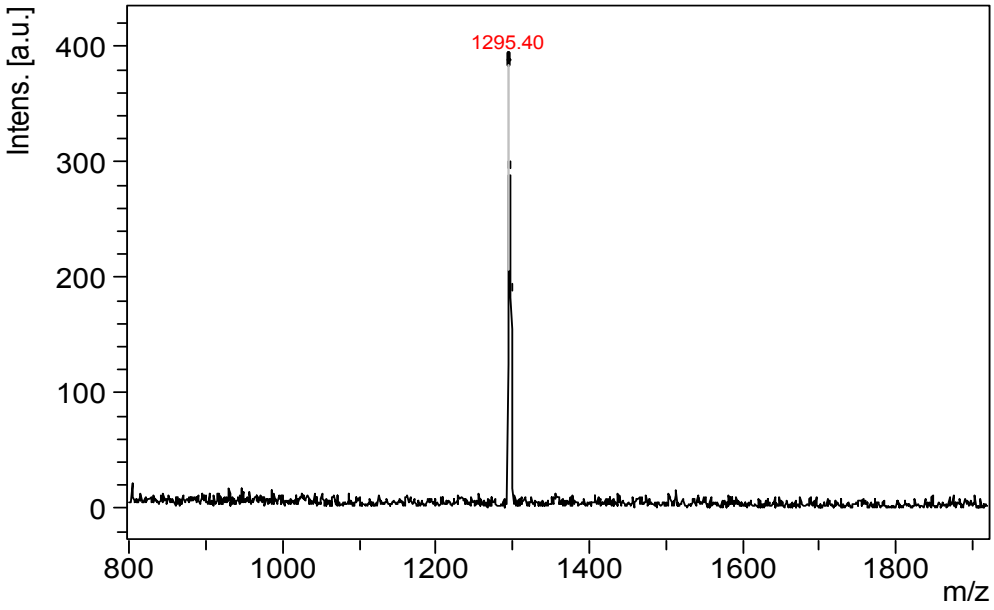
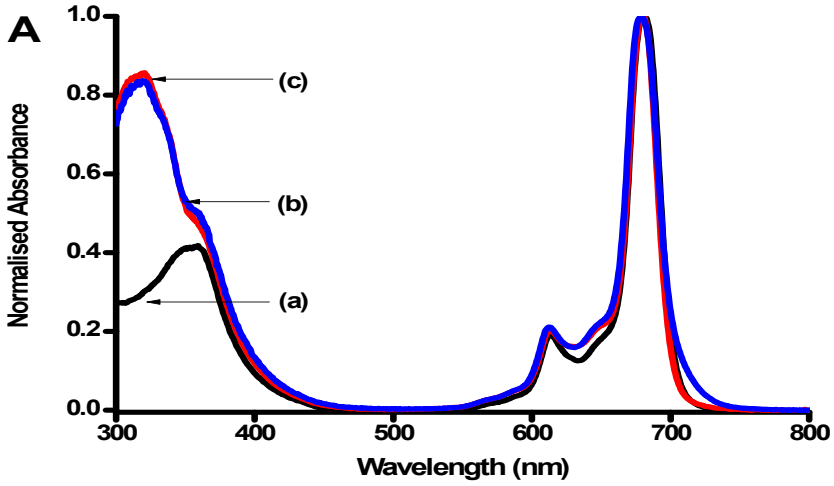


Fig .S2. MS (MALDI-TOF) of complex **3**.



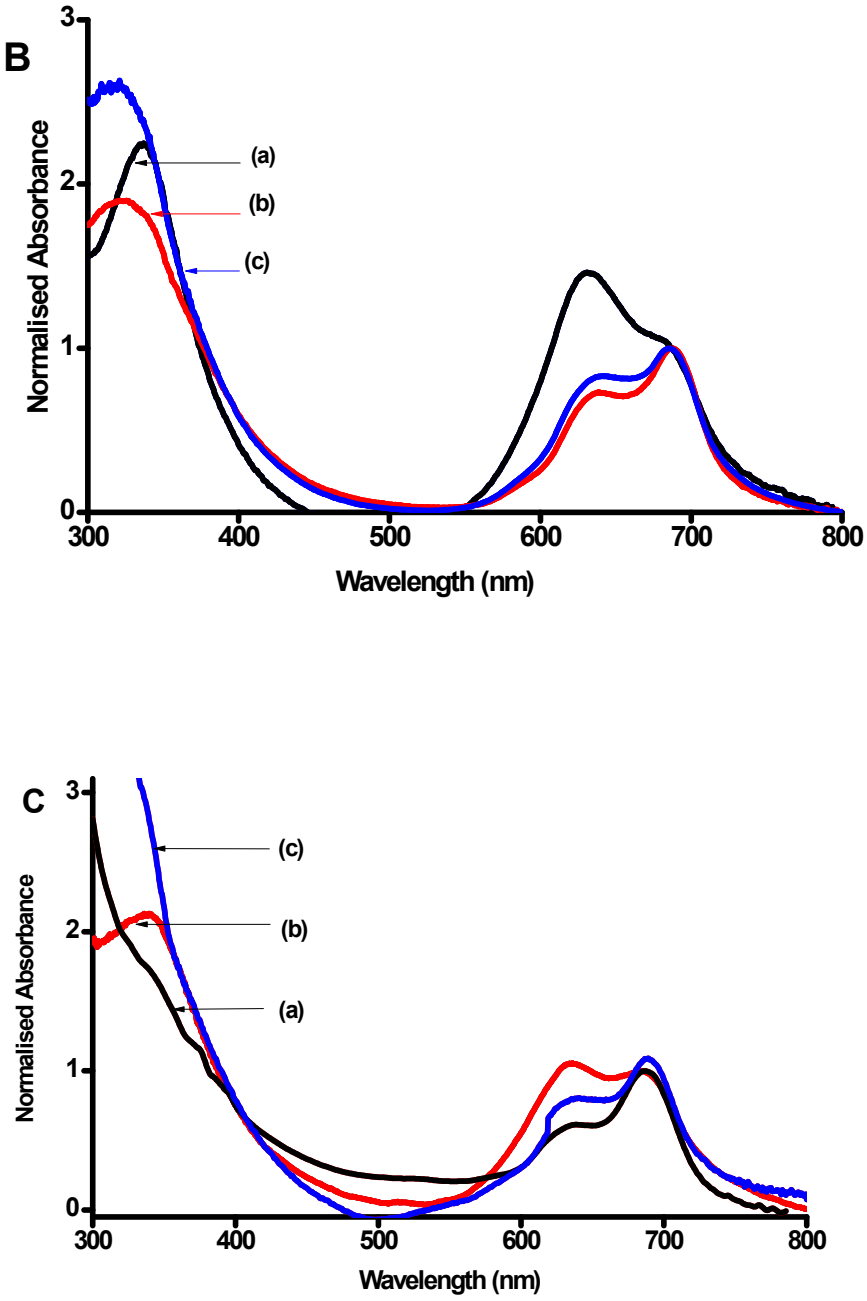


Fig. S3. UV-vis absorption of complexes **3** (a), **4** (b) and **5** (c) in (A) DMSO, and (B) water containing 0.5% DMSO. (C) represents the absorption spectra of **3**-AuNT (a), **4**-AuNT (b) **5**-AuNT (c) in water containing 0.5% DMSO.

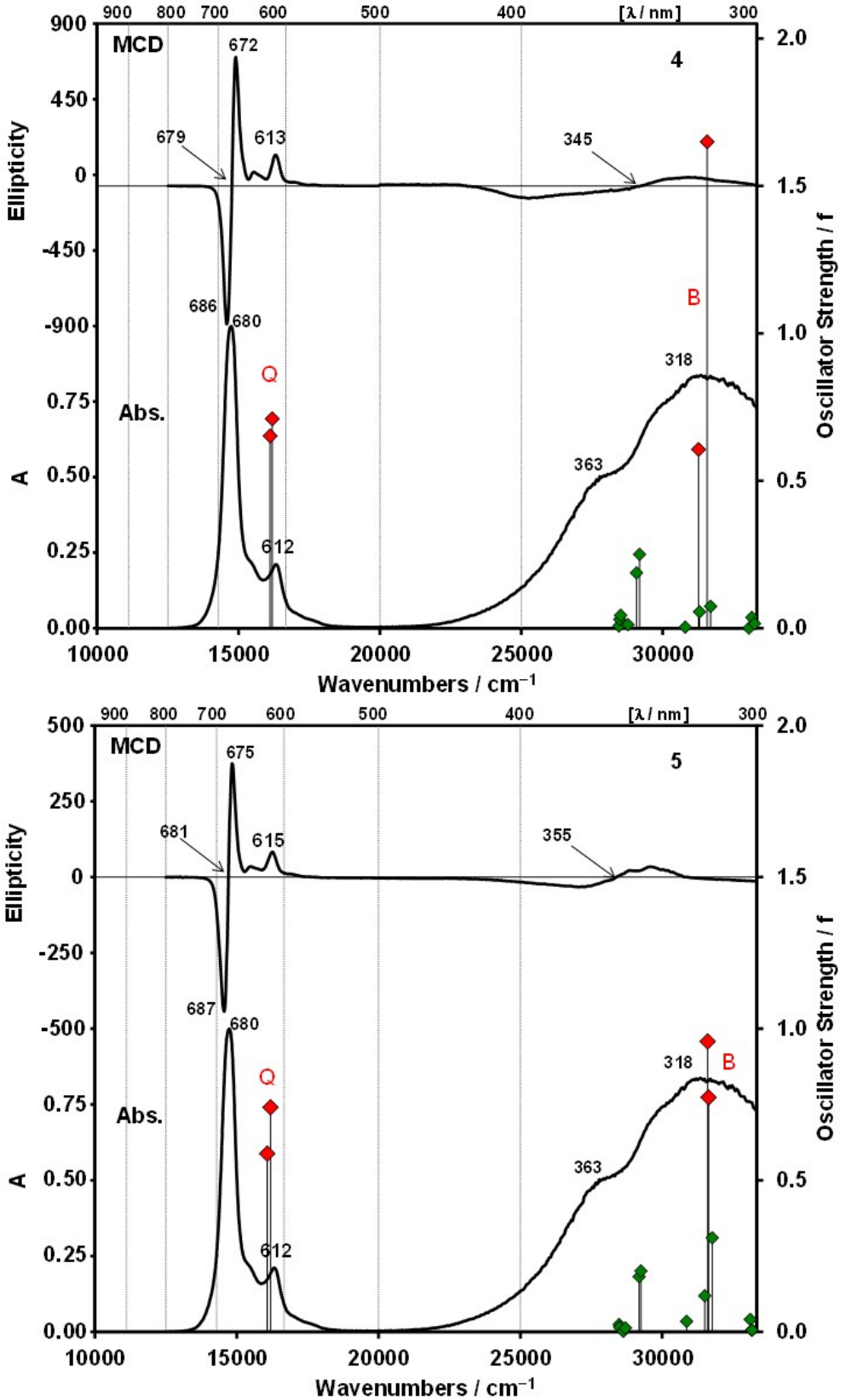


Fig. S4. Absorption and MCD spectra of complexes **4** and **5** in DMSO. The calculated TD-DFT spectrum of the 4-fold symmetric isomers of **4** and **5** are plotted against a secondary axis. Red diamonds are used to highlight bands associated with the Q and B bands of Gouterman's 4-orbital model.

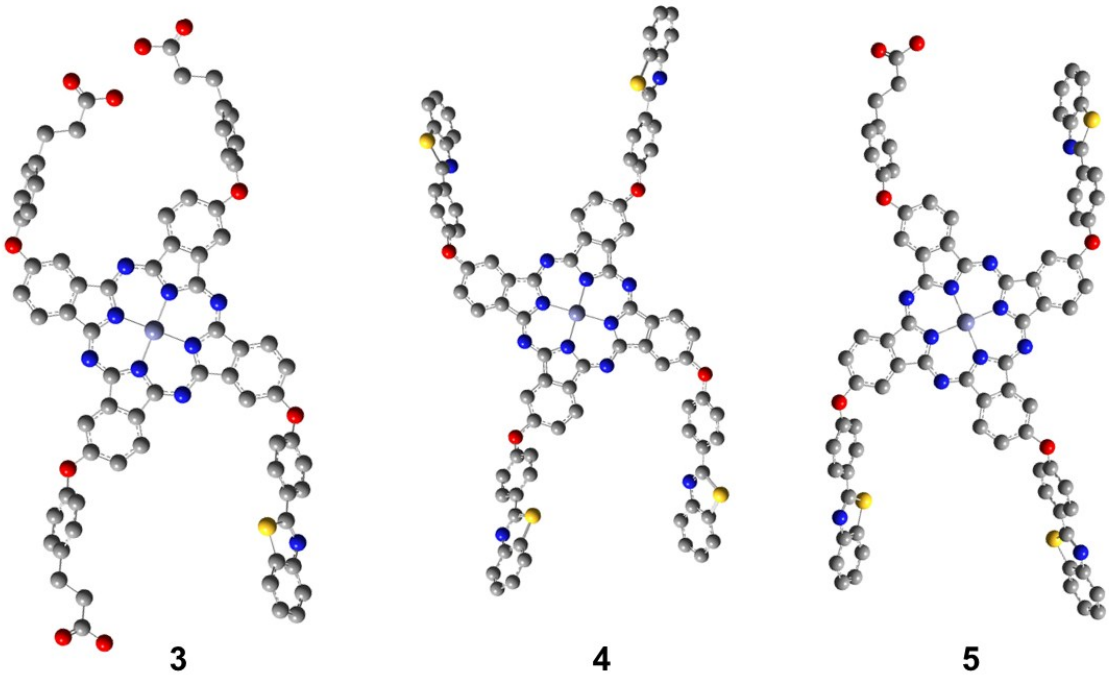
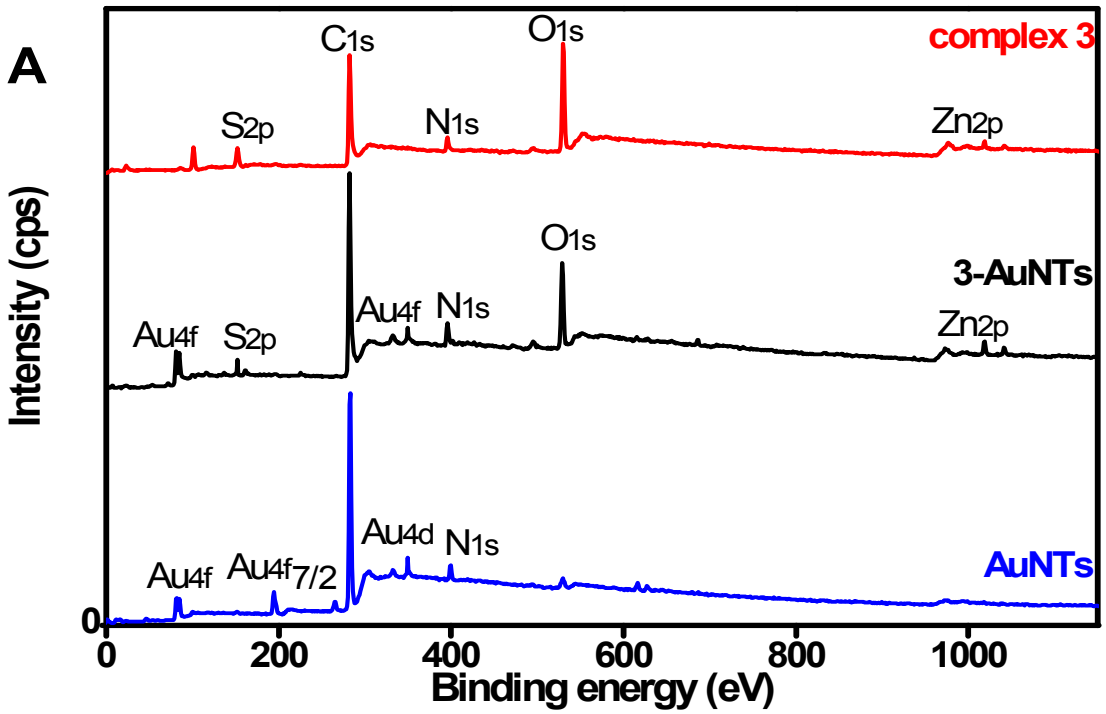


Fig. S5. Optimized geometries of the 4-fold symmetric isomers of **3-5** at the B3LYP/6-31G(d) level of theory.



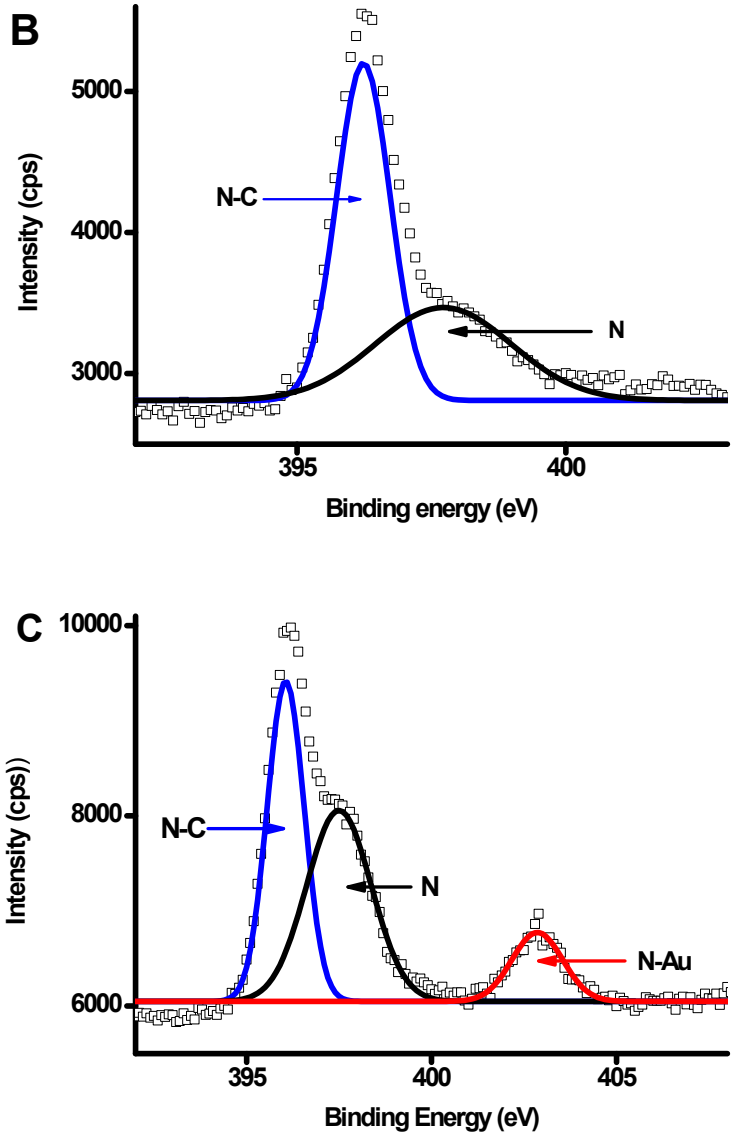


Fig. S6. XPS spectra: (A) survey spectra of complex **3, 3**-AuNTs, AuNTs and high resolution spectra (B) N 1s for complex **3**, (C) N 1s for **3**-AuNTs.

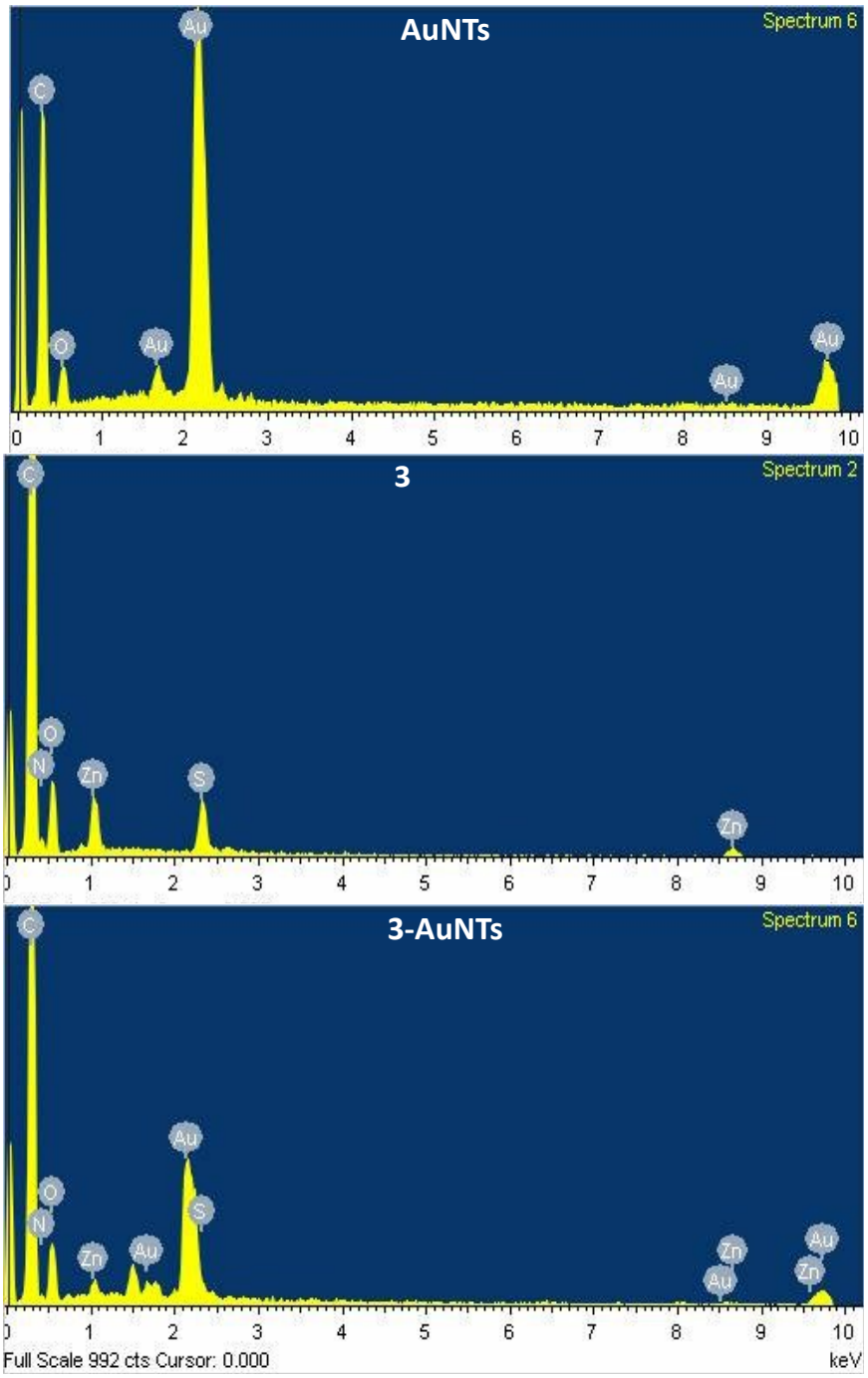


Fig. S7. EDX spectra for AuNTs, complex **3** and **3**-AuNTs (as examples).

Table S1. TD-DFT spectra of the B3LYP optimized geometries for **3**-**5** calculated with the CAM-B3LYP functional and 6-31G(d) basis sets.

				3			
Band[a]	**#[b]**		**Calc[c]**		**Exp[d]**		**Wave Function[e] =**
Q	**1**	16.0	624	(0.55)	14.7	681	**94% a→-a/-s**; …
	2	15.7	616	(0.68)			**93% a→-a/-s**; …
B	**12**	30.9	310	(0.78)	27.9	359	45% H−3^{BT}→-a/-s; **26% s→-a/-s**; …
	13	30.9	309	(0.80)			**66% s→-a/-s**; ……
				4			
Band[a]	**#[b]**		**Calc[c]**		**Exp[d]**		**Wave Function[e] =**
Q	**1**	16.1	620	(0.65)	14.7	680	**94% a→-a/-s;**…
	2	16.2	618	(0.71)			**94% a→-a/-s;**…
B	**10**	31.3	320	(0.61)	27.5	363	55% H−4^{BT}→-a/-s; 18% H−9^{BT}→-a/-s; **8% s→-a/-s**; …
	12	31.6	317	(1.65)			42% H−2^{BT}→-a/-s; **27% s→-a/-s;** 14% H−4^{BT}→-a/-s; …
				5			
Band[a]	**#[b]**		**Calc[c]**		**Exp[d]**		**Wave Function[e] =**
Q	**1**	16.2	622	(0.59)	14.7	680	**93% a→-a/-s;**…
	2	16.4	617	(0.74)			**93% a→-a/-s;**…
B	**11**	30.4	316	(0.96)	28.1	363	38% H−3^{BT}→-a/-s; 13% H−8^{BT}→-a/-s; 9% H−4^{BT}→-a/-s; **8% s→-a/-s**; …
	12	30.9	316	(0.77)			48% H−1^{BT}→-a/-s; **25% s→-a/-s;** …

a − Band assignment described in the text. b − The number of the state assigned in terms of ascending energy within the TD-DFT calculation. c − Calculated band energies (10^3.cm^{-1}), wavelengths (nm) and oscillator strengths in parentheses (f). d− Observed energies (10^3.cm^{-1}) and wavelengths (nm). e − The wave functions based on the eigenvectors predicted by TD-DFT with one electron transitions associated with Gouterman's 4-orbital model highlighted in bold. The **a**, **s**, **-a** and **-s** terminology of Michl[S1] is adopted in this context, which correspond to MOs with $1a_{1u}$, $1a_{2u}$ and $1e_g$* symmetry within Gouterman's 4-orbital model, respectively, if the ligand had D_{4h} symmetry. Only one-electron transitions that contribute at least 10% are included. BT as a superscript denotes an MO that is largely localized on the aminophenoxy substituents.

References

[S1] Michl, J. *Tetrahedron* **1984**, *40*, 3845-3934.