Supplementary Material (ESI) for *PCCP*

Supporting Information

Chromatic Materials for Responsive Surface-Enhanced Resonance Raman Scattering Systems: A Nanometric pH sensor

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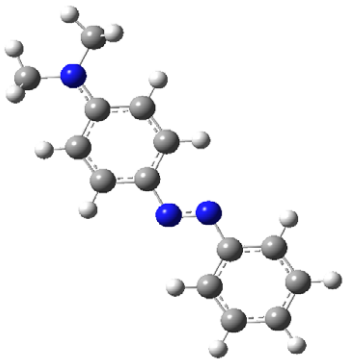
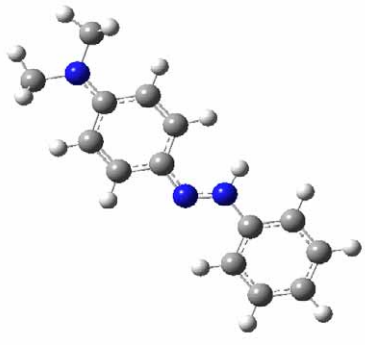
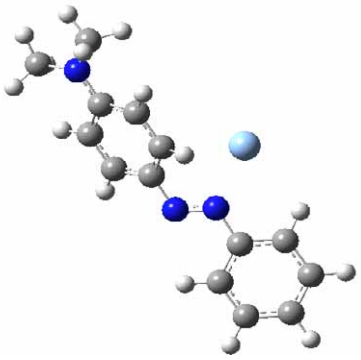
1. Molecular structure of MY, P-MY, MY-Ag and P-MY-Ag



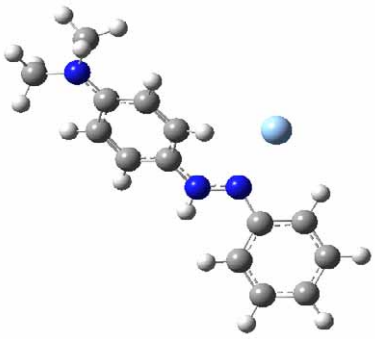
MY



P-MY

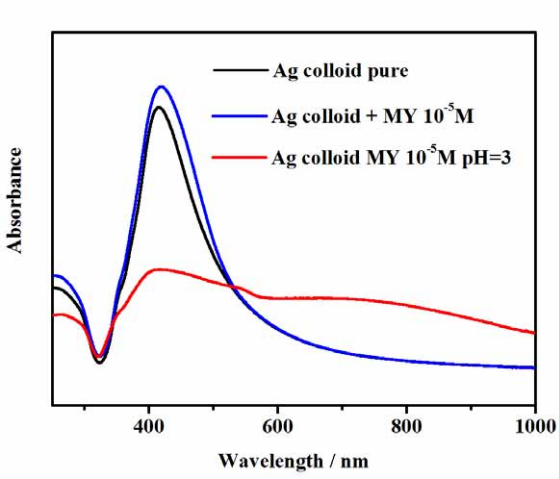


MY-Ag



P-MY-Ag

2. Absorption spectra of pure silver colloid (black line), with addition of MY at 10^{-5} M (blue line), and with addition of HCl (red line).



The UV-Vis spectra of the aggregated colloid (red line) was obtained 15 min after the addition of the $HCl_{(aq)}$ and the corresponding SERS spectrum immediately obtained afterwards. Even though no stabilizing agent was used (to not interfere in the acid-base equilibrium) the colloid remained stable for several hours in the pH range investigated and no change in the Raman relative intensities was observed.

3. Calculated Raman and electronic spectra of MY, P-MY, MY-Ag and P-MY-Ag

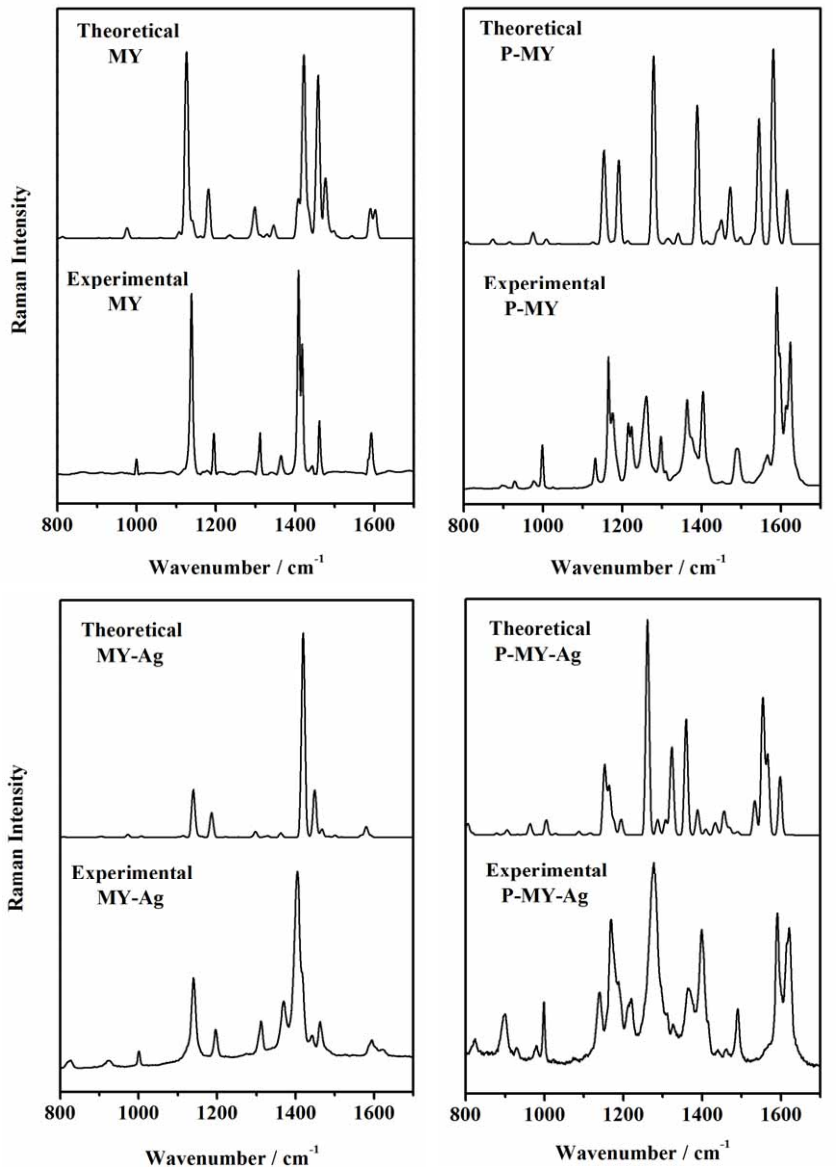
Calculation details

The quantum chemical calculations were performed with the aid of the GAUSSIAN 03 software for the 4-(dimethylamino)-azobenzene (MY) in neutral and monoprotonated forms. The ground states geometries were fully optimized employing the density functional theory (DFT) with the B3LYP hybrid functional (Becke's gradient-corrected exchange correlation in conjunction with the Lee-Yang-Parr correlation functional with three parameters) and the 6-31G(d) one-electron atomic basis sets. The calculations of the molecules attached to Ag atom were performed using the "gen" keyword where the light atoms (CHN) were calculated with the 6-31G(d) basis set and the Ag atom with the LANL2DZ basis set. The nuclear frameworks were assumed to be of C_s symmetry with the molecules placed in the xy plane. The vibrational frequency analyses were carried and no imaginary frequencies were found, indicating that the optimized geometries were in a minimum of the potential energy surface. Finally, at the optimized ground state geometries, the time-dependent density functional theory (TDDFT), with identical hybrid functional and atomic basis sets, was used to calculate the vertical electronic excitation energies of the six low-lying singlet excited electronic states and the corresponding oscillator strengths.

The calculated Raman spectra were plotted using the Maple 9.5 software from an analysis code developed by Daniel J. Ross. The bandwidth chose was 5 cm^{-1} and the

scaling factor used was 0.9594 which is commonly considered for the 6-31G(d) basis set in DFT method.

Experimental and theoretical Raman spectra of MY, P-MY, MY-Ag and P-MY-Ag



The experimental Raman spectra were obtained using the following conditions: MY and P-MY (solid state samples excited at λ_0 = 1064 nm); MY-Ag and P-MY-Ag (SERRS spectra in Ag colloid excited at λ_0 = 514 nm and λ_0 = 633 nm, respectively).

Assignment of the vibrational modes of MY, P-MY, MY-Ag and P-MY-Ag

Methyl-Yellow (MY)

Wavenumber		**MY**
Experimental	Calculated	Assignment
1000	976	ring mode (12)
1139	1126	C-N_{azo} stretching + C-H bending
1195	1181	C-N_{azo} stretching + C-H bending + ring deformation
1312	1298	C-H bending of ring
1365	1346	C-N stretching + ring mode
1409	1408	CH_3 umbrella
1418	1422	N=N stretching + CH_3 umbrella + C-H bending
1443	1452	CH_3 umbrella + C-H bending
---	1458	ring mode + N=N stretching
1462	1477	ring mode + N=N stretching
1586	1590	ring mode (8a)
1592	1602	ring mode (8a)

Protonated Methyl-Yellow (P-MY)

Wavenumber		**P-MY**
Experimental	Calculated	Assignment
928	915	H_3C-N-CH_3 symmetric stretching + ring breathing
976	975	C-H wagging
998	1008	ring breathing
1132	1125	C-H bending + ring mode
1165	1154	C-H bending + C-N_{azo} stretching
1176		C-H bending + C-N_{azo} stretching
1215	1191	C-N_{azo} stretching + C-H bending
1261	1279	C-N-N-C stretching + ring mode
1297	1312	C-H bending + rings mode + C-N-N-C bending
1363	1340	ring mode + C-H bending + H_3C-N-CH_3 stretching
1403	1389	N-N stretching + N-H bending + C-H bending
1490	1472	ring mode + C-H bending
1566	1545	N-H bending + ring mode
1590	1581	ring mode (8a)
1623	1615	ring mode (8a) + N-H bending + N-N stretching

Methyl-Yellow – Ag (MY-Ag)

Wavenumber		**MY-Ag**
Experimental	Calculated	Assignment
1000	972	ring mode (12)
1140	1140	C-N_{azo} stretching + C-H bending
1197	1186	C-N_{azo} stretching + C-H bending
1312	1298	C-H bending
1370	1362	C-N stretching + ring mode + C-H bending
1405	1420	N=N stretching
1441	1449	ring mode + N=N stretching
1463	1467	ring mode + N=N stretching
1594	1580	ring mode (8a)
1622	1591	ring mode (8a) + C-N stretching

Protonated Methyl-Yellow – Ag (P-MY-Ag)

Wavenumber		**P-MY-Ag**
Experimental	Calculated	Assignment
824	805	N-H bending + ring breathing
900	905	H_3C-N-CH_3 stretching + ring breathing
980	964	ring mode (12)
999	1005	ring breathing
1140*		
1169	1153	CH_3 wagging + CH bending + C-N_{azo}
1188*		
1221	1194	C-H bending
1278	1262	C-N-N-C stretching + ring mode
1326	1323	N-H bending + N-N stretching + ring mode
1367	1360	N-N stretching + N-H bending + ring mode
1400*		
1491	1489	ring mode (15)
1592	1555	ring mode (8a) + N-H bending
1621	1598	ring mode (8a) + N-H bending

* modes assigned to the neutral species

Experimental (UV-Vis) and calculated vertical transition energies (TDDFT) of the first allowed electronic excitation of MY, P-MY, MY-Ag and P-MY-Ag

Molecule	Experimental* / nm	Theoretical / nm (oscillator strength)
MY	411	385 (f = 0.9359)
P-MY	515	446 (f = 1.0536)
MY-Ag	---	479 (f = 0.4061)
P-MY-Ag	---	519 (f = 0.8931)