# Electronic supplementary information

## Surface-enhanced Raman scattering studies of rhodanines: evidence for substrate surface-induced dimerization

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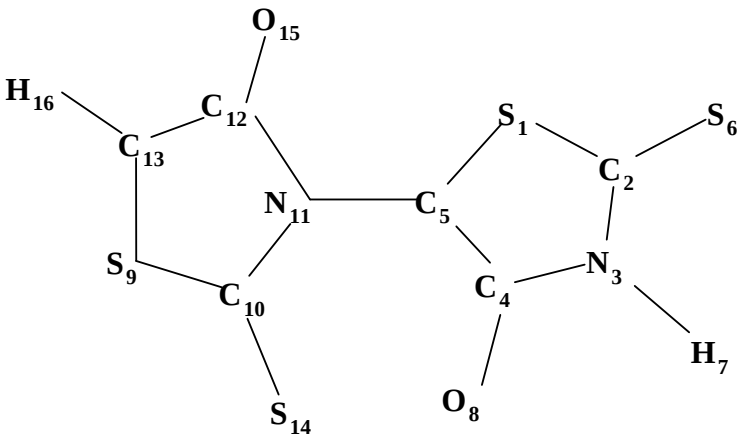
**Table S1.** TD-DFT (B3-LYP/cc-pVDZ) calculations of the five lowest energy singlet electronic transitions of the *Z* isomer Rd dimer. Orbital 63 is the HOMO and orbital 64 is the LUMO.

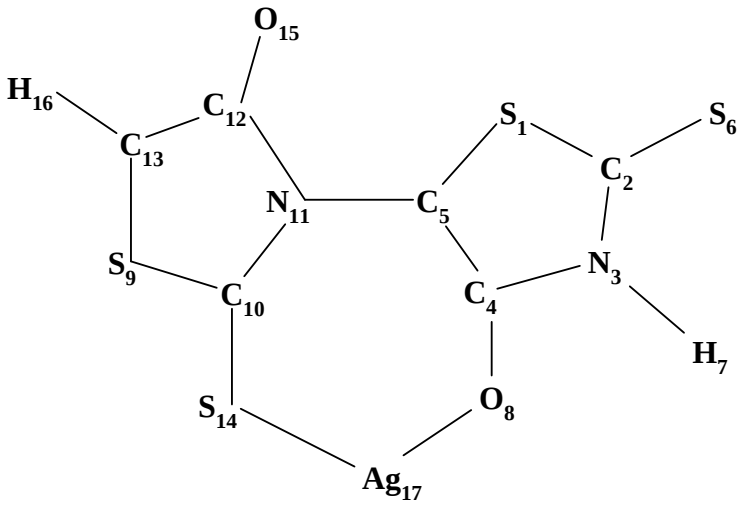
| Excited state no. | Symmetry | Orbital transitions | Contributions | λ / nm | *f* |
|---|---|---|---|---|---|
| 1 | $^1$A" | 61→64<br>61→65<br>62→64<br>62→65 | 0.12788<br>-0.13112<br>0.64489<br>0.16180 | 421.62 | 0.0001 |
| 2 | $^1$A" | 61→64<br>61→65<br>62→64<br>62→65 | 0.64322<br>-0.16032<br>-0.12490<br>-0.14041 | 417.21 | 0.0000 |
| 3 | $^1$A' | 63→64 | 0.62710 | 359.25 | 0.5750 |
| 4 | $^1$A' | 60→64<br>63→65 | 0.64045<br>0.16570 | 319.42 | 0.0551 |
| 5 | $^1$A" | 58→64<br>61→65<br>62→64<br>62→65 | 0.13568<br>-0.21313<br>-0.22380<br>0.58328 | 306.33 | 0.0000 |

**Table S2.** TD-DFT (B3-LYP/cc-pVDZ) calculations of the ten lowest energy singlet electronic transitions of the *E* isomer Rd ($N^+$=C) dimer. Orbital 66 is the HOMO and orbital 67 is the LUMO.

| Excited state no. | Symmetry | Orbital transitions | Contributions | λ / nm | *f* |
|---|---|---|---|---|---|
| 1 | $^1$A' | 66→67 | 0.36127 | 4602.29 | 0.0040 |
| 2 | $^1$A" | 65→67 | 0.65953 | 1210.00 | 0.0000 |
| 3 | $^1$A" | 64→67 | 0.68489 | 781.35 | 0.0000 |
| 4 | $^1$A" | 62→67 | 0.69749 | 529.05 | 0.0003 |
| 5 | $^1$A' | 61→67<br>66→68 | 0.30855<br>0.60015 | 468.66 | 0.0835 |
| 6 | $^1$A' | 63→67<br>66→69 | 0.58333<br>-0.27489 | 433.23 | 0.1401 |
| 7 | $^1$A' | 61→67<br>63→68<br>66→68<br>66→69 | 0.55943<br>-0.10577<br>-0.24284<br>0.11266 | 393.25 | 0.0773 |
| 8 | $^1$A" | 59→67<br>65→68<br>65→69 | 0.41087<br>0.52244<br>0.16828 | 390.51 | 0.0001 |
| 9 | $^1$A' | 60→67<br>63→67<br>66→69 | 0.17660<br>0.16732<br>0.59846 | 362.66 | 0.0508 |
| 10 | $^1$A" | 59→67<br>65→68<br>65→69 | 0.55181<br>-0.40823 | 362.53 | 0.0000 |




Rd dimer




Rd dimer ($Ag^{+}$)/Rd dimer($Ag^{0}$)

**Fig. S1** Calculated structures for the hypothetical ("polymer"/$N^{+}$=C) Rd dimers formed by the interaction of the NH of one monomer with the methylene moiety of another monomer in the absence and presence of silver nanoparticles ($Ag^{+}$ and $Ag^{0}$). The corresponding calculated SERS spectra are shown in Fig. S2.

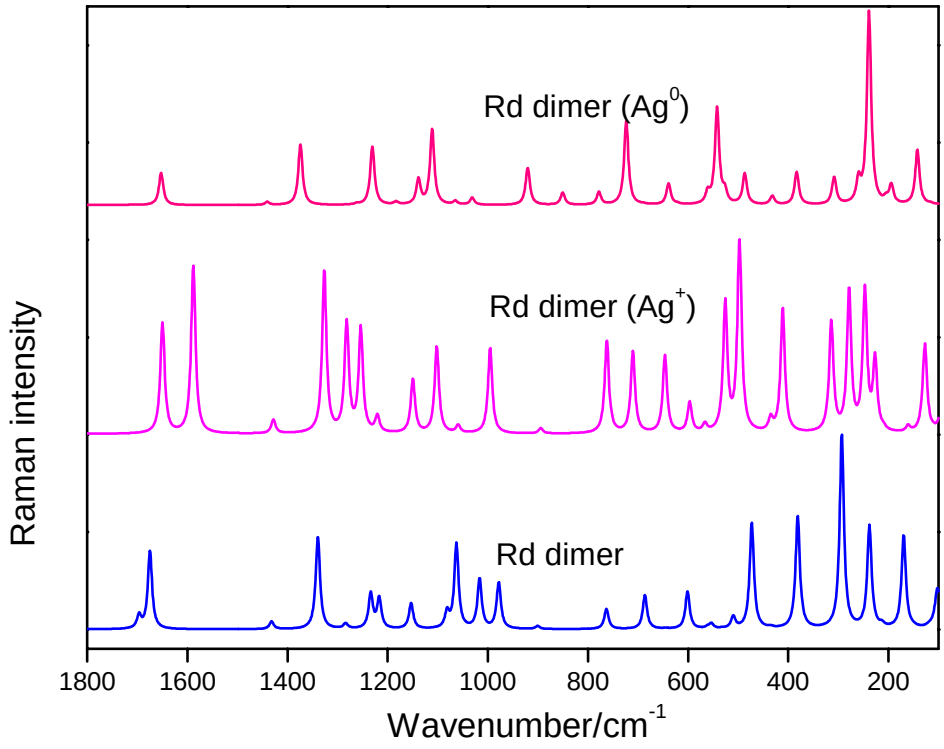



**Fig. S2** Calculated SERS spectra for the hypothetical ("polymer"/$N^+$=C) Rd dimers shown in Fig. S1.