Electronic Supplementary Information

Distinguishing Binding Modes of a New Phosphonium Dye with DNA by Surface-Enhanced Raman Spectroscopy

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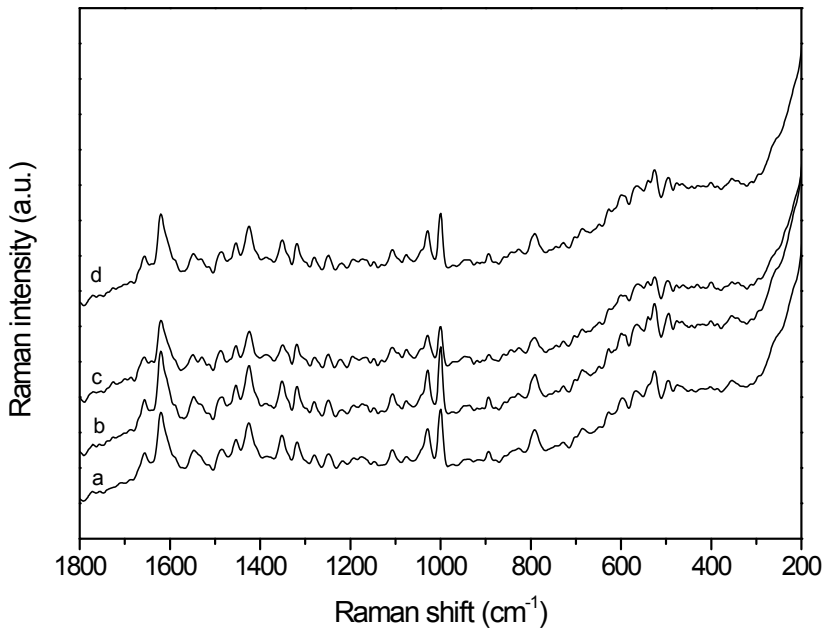


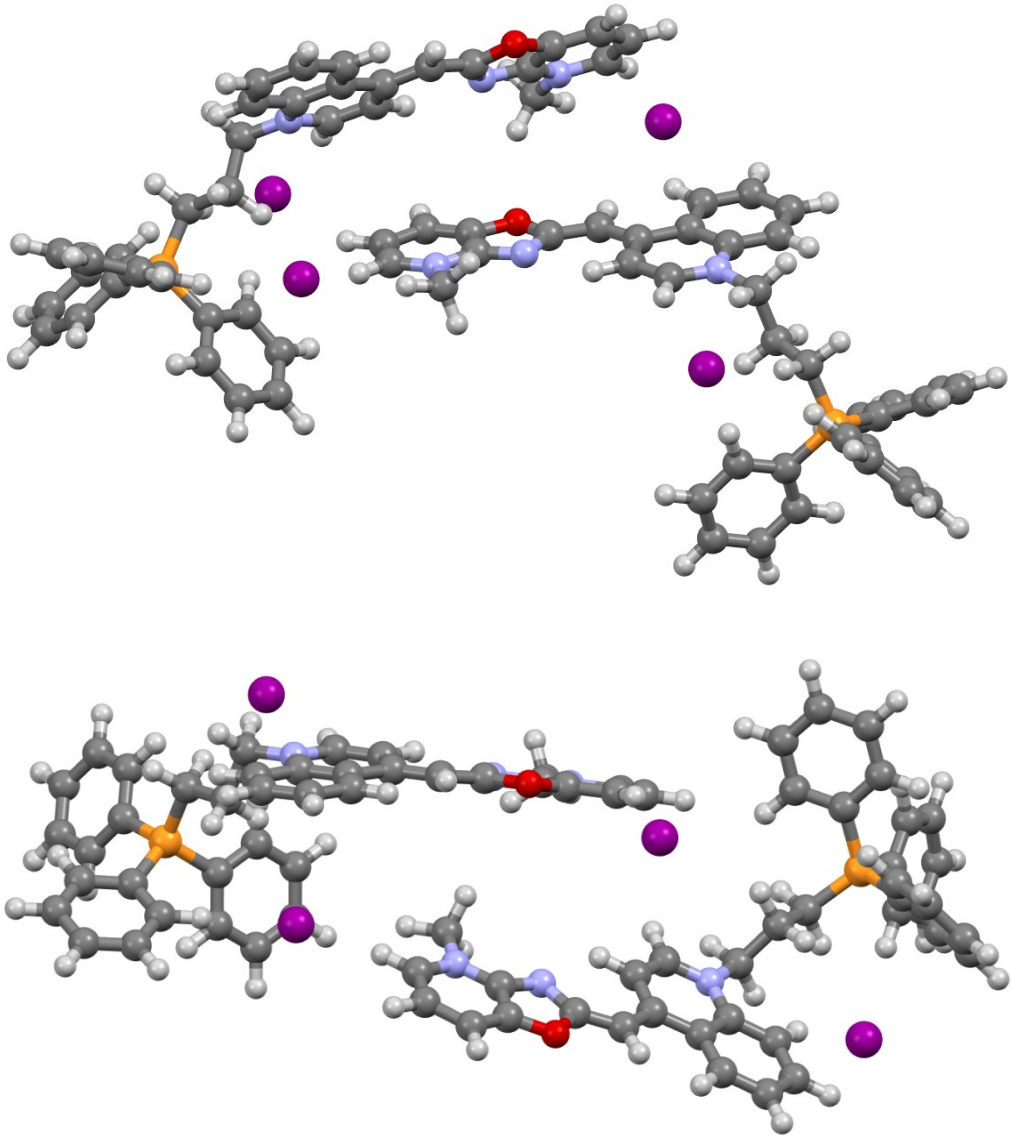
Figure S1. SERS spectra of the phosphonium dye/AT polynucleotide complex ([dye]/[poly dAdT–poly dAdT] = 1/10, c(dye) = 5.0×10^{-6} mol/L) in the silver colloid: three samples prepared in the same way (a, b and c) and the averaged spectrum (d). Excitation at 1064 nm. The spectra are displaced for visual clarity.

Table S1. Relative free energies and Boltzmann populations of the investigated conformers of the dye in gas-phase at B3LYP/6-31G(d) level of theory

Conformer	Δ*G* (kcal/mol)	Boltzmann populations (%)
c1	5.22	0.01
c2_3	4.09	0.06
c2_2	1.93	2.12
c2_1	0.15	42.75
c2_0	0.00	55.07

Table S2. B3LYP/pc-2 calculated ^{1}H NMR chemical shifts for the c1 and c2 conformers in DMSO

NMR data	^{1}H NMR chemical shift (ppm)			
	Experimental[1]	Calculated		
		$c1^{2+}$	$c2^{2+}$	$c2^{0}$
m (2H, CH_2)	2.07, 2.12	1.99, 2.41	1.98, 2.21	1.58, 1.95
m (2H, CH_2P^+)	3.73, 3.78	2.98, 2.98	2.97, 3.06	2.64, 2.64
t (2H, N–CH_2)	4.63	4.36	4.41	2.31, 2.73
s (3H, N–CH_3)	4.2	4.15	4.09	2.66
s (1H, CH)	6.53	6.24	6.75	4.58
m (24H, Ar)	7.35–8.54	6.96–8.33	7.31–8.76	4.45–8.32
H53	-	11.46	8.67	5.39



Scheme S1. B3LYP/gen optimized geometries of the phosphonium dye – 2I dimers (H C N O – 6-31G(d,p); I – SDB-cc-pVTZ basis set and ECP) (same orientation (top), opposite orientation (bottom)).

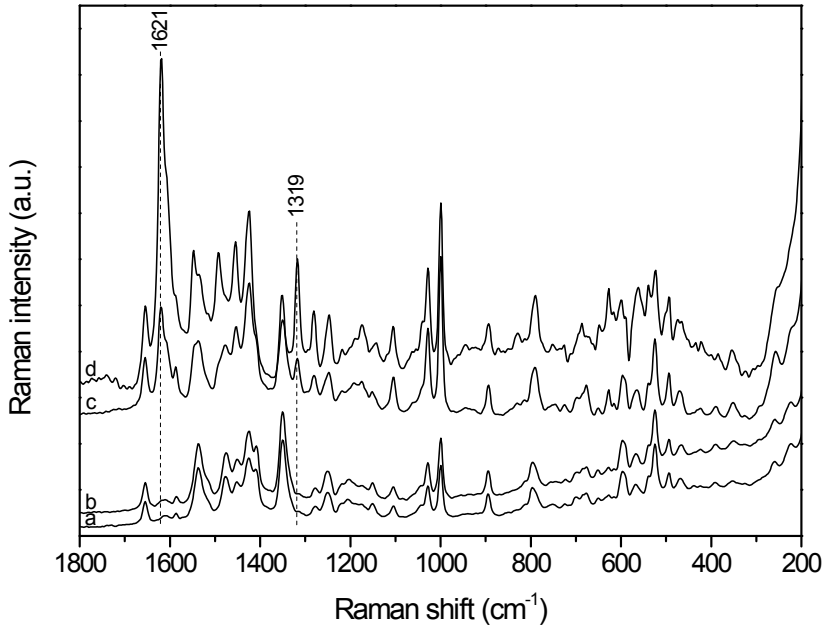


Figure S2. SERS spectra of the phosphonium dye during time: a) 5.0×10^{-5} mol/L after 2 min, b) 5.0×10^{-5} mol/L after 50 min, c) 5.0×10^{-6} mol/L after 2 min, and d) 5.0×10^{-6} mol/L after 50 min. Excitation at 1064 nm. The spectra are displaced for visual clarity. The baseline of the SERS spectrum (d) was corrected.

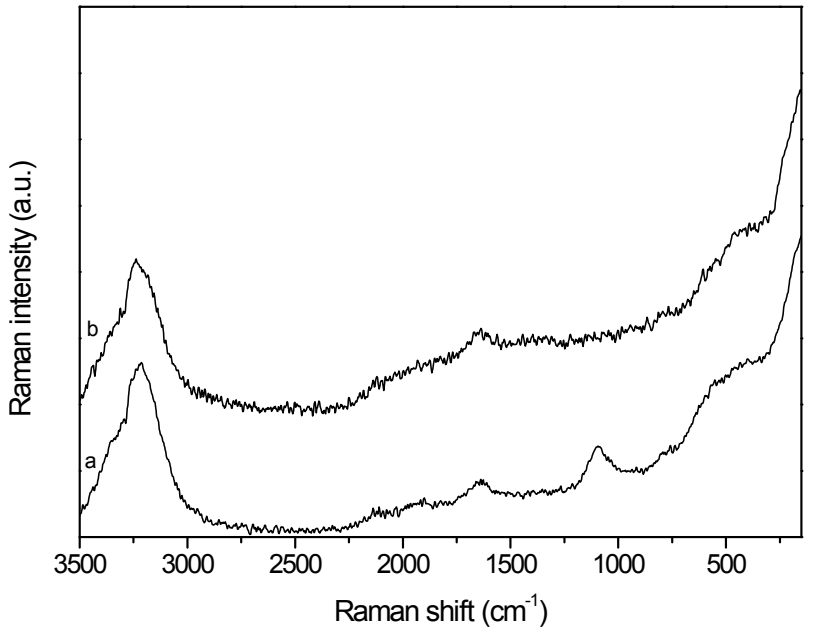


Figure S3. SERS spectra of: a) the silver colloid and b) the silver colloid containing poly dA–poly dT, $c = 1.0\times10^{-5}$ mol/L.

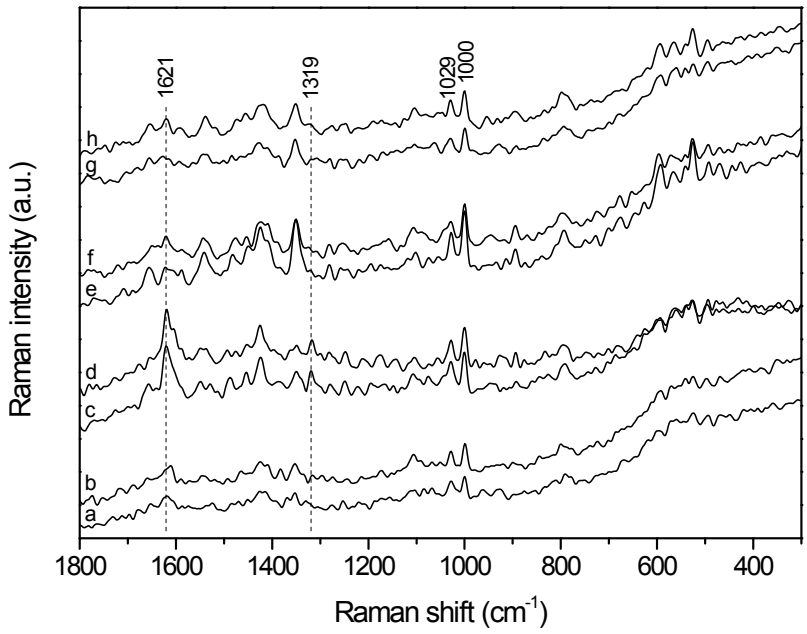


Figure S4. SERS spectra of the phosphonium dye/AT polynucleotide complexes during time: a) [dye]/[poly dA–poly dT] = 1/10 after 2 min, b) [dye]/[poly dA–poly dT] = 1/10 after 50 min, c) [dye]/[poly dAdT–poly dAdT] = 1/10 after 2 min, d) [dye]/[poly dAdT–poly dAdT] = 1/10 after 50 min, e) [dye]/[poly dA–poly dT] = 1/2 after 2 min, f) [dye]/[poly dA–poly dT] = 1/2 after 50 min, g) [dye]/[poly dAdT–poly dAdT] = 1/2 after 2 min, and h) [dye]/[poly dAdT–poly dAdT] = 1/2 after 50 min; $c(\text{dye})_{\text{complex}} = 5.0\times10^{-6}$ mol/L. Excitation at 1064 nm. The spectra are displaced for visual clarity.

References

(1) L.-M. Tumir, I. Crnolatac, T. Deligeorgiev, A. Vasilev, S. Kaloyanova, M. Grabar Branilović, S. Tomić and I. Piantanida, *Chem. Eur. J.*, 2012, **18**, 3859–3864.