Electronic Supplementary Information

Surface Amplification of Tetraphenylporphyrin Overtone and Combination Raman Bands in Drop Coating Deposition Raman (DCDR) on Electrically Conductive Surfaces

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Figure S1. (a) Raman spectra of 1×10^{-4} M TPP at various substrate activation temperatures. (b) The S/N ratio of Raman signal at 827 cm⁻¹, a typical TPP vibrational mode assigned as the wagging of H atom in phenyl rings, shows an enhancement with the substrate activation temperature.



Figure S2. Raman spectra of background signal on (a) Au, (b) Al, (c) Ta, and (d) ITO substrates.



Figure S3. AFM texture, roughness, waviness surface profiles of various bare conductive substrates: (a) gold, (b) aluminium, (c) tantalum, and (d) tin-doped indium oxide (ITO). Ra, Rq, Wa, and Wq are the arithmetic mean height of the primary profile, the root-mean-square height for the primary profile, the arithmetic mean waviness, and the root-mean-square waviness, respectively.

Band (cm ⁻¹)	Vibrational mode ¹⁻⁴	Symmetry ^{3,4}
336	Stretching (pyrrole translation)	Ag
430	In-plane bending(pyrrole rotation)	B _{2u}
497	Out-of-plane C_{β} -H and C_m -H	-
543	out-of-plane bending $(C_{\alpha}-C_m)$	Au
637	Diagonal expansion of phenyl rings	A_{g}
827	δ (pyrrole deformation) asymmetric	B_{1g}
869	δ (pyrrole deformation)asymmetric	B_{1g}
960	v(pyrrole breath)	Ag
1000	Pyrrole breathing and phenyl	Ag
1075	$\delta(C_b-H)$ symmetry	Ag
1137	Symmetric stretching of the C_{α} - C_m - C_{φ}	-
	bonds	
1241	$\delta(C_b-H)$ asymmetric	B_{1g}
1328	v(pyrrole quarter-ring)	B_{1g}
1440	Rocking of the H atom on the phenyl	А
	rings and Symmetric Stretching $(C_{\beta}-C_{\beta})$	
1458	$\nu(C_{\alpha}-C_m)$ sym	Ag
1500	$\nu(C_{\beta}-C_{\beta})$	$\overline{A_g}$
1553	$v(C_{\alpha}-C_m)$ asymmetric	B _{1g}
1576	$v(C_{\alpha}-C_m)$ asymmetric	Ag

Table S1. The Raman vibrational mode of TPP

Table S2. Electrical conductivity of DCDR substrates

Substrate	Electrical Condcutivity (S/m) ⁵⁻⁸
Au	4.87×10^{7}
Al	4.13×10^{7}
Та	8.19×10^{6}
ITO [*]	6.49×10^{5}

^{*)}ITO glass with a sheet resistance of 7 Ω / \Box and ITO thickness of 2200±300 Å

Table S3. Observed Raman emission anisotropy of TPP vibrational peaks after subtracted by fluorescence baseline

Vibrational peak (cm ⁻¹)*	r'(YY)(YX)	r'(XX)(XY)	Symmetry*
826	0.1904	0.1655	B_{1g}
961	0.0925	0.1151	Ag
1002	0.1133	0.2299	Ag
1083	0.0823	0.1108	Ag
1138	0.0505	0.0373	-
1240	0.1105	0.0324	B _{1g}
1331	0.0711	-	B _{1g}
1459	0.0465	-0.0231	Ag

*)Assignments of vibrational mode and symmetry are based on Table S1.



Figure S4. DCDR spectra on Au substrate prepared from 1×10^{-4} M TPP solution in chloroform and recorded at the various laser excitation wavelength. All spectra were recorded for 45 s of acquisition time with 5× of co-addition and excited with the minimum laser power of 0.4, 0.2, and 1 mW at 488, 532, and 785 nm, respectively. All samples were activated at 100 °C for 10 minutes prior to the Raman measurements.



Figure S5. Conventional Raman spectrum of 1×10^{-4} M TPP solution in chloroform inside a glass capillary with respect to its DCDR spectrum prepared on Au substrate from 1×10^{-4} M TPP solution in chloroform. The strong peaks under the bracket are assigned to chloroform vibrational modes. The inset shows the magnified conventional Raman spectrum depicting typical vibrational modes of TPP. DCDR sample was activated at 100 °C for 10 minutes prior to the Raman measurement.

References

- 1 Gorski, A.; Starukhin, A.; Stavrov, S.; Gawinkowski, S.; Waluk, J. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. **2017**, 173, 350–355
- 2 Bell, S. E. J.; Al-Obaidi, A. H. R.; Hegarty, M. J. N.; McGarvey, J. J.; Hester, R. E. J. Phys. Chem. **1995**, 99, 3959-3964
- 3 Aydin, M. Vibrational Spectroscopy. 2013, 68, 141–152.
- 4 Saini, G. S. S. Spectrochimica Acta Part A, 2006, 64, 981-986.
- 5 Matula, R. A. J. Phys. Chem. Ref. Data. 1979, 8, 1147-1298.
- 6 Desai, P. D.; Chu, T. K.; James, H. M.; Ho, C. Y. J. Phys. Chem. Ref. Data, 1984, 13, 1069-1096.
- 7 Desai, P. D.; James, H. M.; Ho, C. Y. J. Phys. Chem. Ref. Data, **1984**, 13, 1131-1172.
- 8 Zhuhai Kaivo Optoelectronic Technology, <u>http://www.zh-kv.com/Upload/DownFiles/</u> 2014.3.30_20.51.34_8974.pdf (June 22th, 2018)