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ELECTRONIC SUPPLEMENTARY INFORMATION

Biological application of water-based electrochemically synthesized CuO leaf-like arrays: SERS response modulated by the positional isomerism and interface type

Received 2th September 2017,
Accepted 00th xxxx 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Cupric oxide leaf-like nanostructures (CuONSs) (the average dimensions of 80 – 180 nm in width and 400 – 750 nm in length) were synthesized by anodic electrochemical dissolution of copper in an ethanol solution containing LiCl electrolyte and water. Ultraviolet-visible (UV-Vis), Fourier-transform infrared (FT-IR), and Raman spectroscopies as well as scanning electron microscope (SEM) and X-ray powder diffraction (XRD) were used to explore the metal surface plasmon, size, rheology, and structure of CuONSs. Then, pyridine α–aminophosphinic acid isomers (*α*–, *β*–, and *γ*–NHPy) were synthesized and assembled on the CuONSs/air and CuONSs/aqueous solution interfaces at pH level of solution = 7. Differences in adsorption and thus, in the spectral response resulting from positional isomerism, were examined by surface-enhanced Raman scattering (SERS) with the 785 nm excitation wavelength. The manner of interaction of the investigated isomers with CuONSs in an aqueous solution was discussed in detail and compared with that at the CuONSs/air interface. For *γ*–NHPy, at the CuONSs/water interface, the time-dependent changes in the spectral profile were observed and analyzed. For *β*–NHPy at the CuONSs/air interface, tip-enhanced Raman scattering (TERS) measurements were performed. These measurements allowed to observe single molecule behavior and avoid interference from molecule' surrounding environment.

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† Electronic Supplementary Information (ESI) available: See
It contains the calculated wavenumbers and potential energy distribution (PED, %) for the FT–RS spectra of the investigated α-aminophosphinic acid derivatives of pyridine (Table S1).
DOI: 10.1039/x0xx00000x

Table S1. The calculated wavenumbers and potential energy distribution (PED, %) for the FT-RS spectra of the α–aminophosphinic acid derivatives of pyridine.

Calculated wavenumbers /cm^{-1}			B3LYP/6-311G(df,p) (PED %; > 5%)
α-PyNH	β-PyNH	γ-PyNH	
402	403		γ_{as}(Ph)(81), ρ_s(C_{Ph}P(O,O)C_α), γ_{as}(Ph)
	405	402	γ_{as}(Py)(81), δ_{oop}(CC(H)C)$_{Py}$
406	410	411	γ_{as}(Ph)(57), γ_{as}(Ph), ρ_s(C_{Ph}P(O,O)C_α)
412		412	γ_{as}(Ph)(71), ρ_s(C_{Ph}P(O,O)C_α)
421		422	ρ_s(C_{Ph}P(O,O)C_α)(18), ρ_r($C_\alpha C_{Py}$(CN_{Py})), ρ_s(C(H,H)C(H,H)CH_3), ρ_s(C(H,H)C(H,H)CH_2), δ(PC_α(C_{Py})N), γ_{as}(Ph)
470	478	471	γ(Ph)(39), δ_{oop}(C(C,C)$_{Ph}$P), γ(Py), γ(CC(P)C)$_{Ph}$, ν(PC_α)
496	497	482	γ(Py)(17), δ_{oop}(C_α(C,C)), ρ_s(CC(H,H)C), ρ_w(C_{Ph}P(O,O)C_α), γ(CC(C)N)$_{Py}$, δ_p(Py)
538	544	535	ρ_w(C_{Ph}P(O,O)C_α)(25), δ_{oop}(C_α(C,C))(11), γ_{as}(Py), γ_{as}(Ph), δ_{as}(Ph), δ_{oop}(C(C,C)$_{Ph}$P), γ(CC(P)C)$_{Ph}$, ν(PC_α), δ_{as}(Ph)
559	566	551	ρ_s(CH_2)(20), δ(PC_α(C_{Py})N), δ_{as}(Py), ρ_r(C(H,H)C(H,H)CH_2), ρ_s(NC(H,H)C), ρ_r(CC(H,H)C), ρ_w(C_{Ph}P(O,O)C_α), δ_{oop}(C_αN(H)C)
625	616		δ_{as}(Py)(56), δ(PC_α(C_{Py})N)
621	621	624	δ_{as}(Ph)(89)
640	643	637	δ_{as}(Py)(40), δ_{oop}(C_αN(H)C), ν(PC_α), δ(PC_α(C_{Py})N), γ(C_{Ph}P(O,OH)C_α), γ(C_αN(H)C)
	675	667	δ_{oop}(C_αN(H)C)(26), ρ_s(C_α(H)C), δ_{as}(Py), ν(C_αN), ν(PC_α), ν(CN)
681		685	γ(C_{Ph}P(O,OH)C_α)(54), δ_{as}(Py), δ_p(Py)
701	702	700	δ_p(Ph)(64), γ(CC(H)C)$_{Ph}$(13), δ_{oop}(CC(H)C)$_{Ph}$
705	710	705	δ_{as}(Ph)(32), ν(C_{Ph}P), δ_p(Ph)
718	721		δ_p(Py)(61), δ_{oop}(CC(H)C)$_{Py}$, δ_{oop}(C_α(C,C)), ν(PC_α), ρ_r(C(H,H)C(H,H)CH_2), ρ_r(C(H,H)C(H,H)CH_3), δ_{as}(Py), δ(PC_α(C_{Py})N)
730	730		ρ_r(CC(H,H)C)(39), ρ_r(CCH_3), δ(PC_α(C_{Py})N), ρ_r(C(H,H)C(H,H)CH_3), ρ_r(C(H,H)C(H,H)CH_2)
	737	740	δ_{oop}(C_αN(H)C)(15), ρ_r(CC(H,H)C), ν(PC_α), δ(PC_α(C_{Py})N), δ_p(Py)
755			γ(CC(H)C)$_{Py}$(45), δ(Py), δ(NC(H)C)$_{Py}$
757	759	753	δ_p(Ph)(33), δ_{oop}(CC(H)C)$_{Ph}$, δ_{oop}(C(C,C)$_{Ph}$P), γ(CC(H)C)$_{Ph}$, γ(CC(P)C)$_{Ph}$
804		806	γ(C_αN(H)C)(19), ν(C_αN), ν($C_\alpha C_{Py}$), δ_p(Py)
809	812		δ_p(Py)(23), γ(CC(C)N)$_{Py}$, γ(CC(H)C)$_{Py}$, ρ_r(NC(H,H)C), ν(CC), ν(PO)
824	822		δ_p(Py)(20), ν(CC), ρ_r(NC(H,H)C), γ(CC(C)N)$_{Py}$, ρ_r(CCH_3), ρ_r(C(H,H)C(H,H)CH_2), ν(PC_α),
			δ_{oop}(CC(H)C)$_{Py}$, δ_{oop}(C_α(C,C))
	826	820	ν(PO)(56), ρ_b(P(OH))
847	839		ρ_r(CCH_3)(17), ρ_r(CC(H,H)C), ν(PO), ν(CN), ν($C_\alpha C_{Py}$), ρ_t(CC(H,H)C), ρ_r(C(H,H)C(H,H)CH_2)
858	859	852	δ_{oop}(CC(H)C)$_{Ph}$(95)
866			ν(PO)(69)
	866	859	ν(CC)(12), ρ_r(CCH_3), ν($C_\alpha C_{Py}$), ρ_s(C_α(H)C), ρ_r(CC(H,H)C)
895		873	δ_{oop}(CC(H)C)$_{Py}$(39), δ_{oop}(C_αN(H)C)
938	936	933	δ_{oop}(CC(H)C)$_{Ph}$(84)
	941		δ_{oop}(CC(H)N)$_{Py}$(43), δ_{oop}(CC(H)C)$_{Py}$, δ_p(Py)
946	948		ρ_r(NC(H,H)C)(24), ρ_r(CCH_3), ρ_t(CC(H,H)C), ρ_t(C(H,H)C(H,H)CH_3), ρ_t(C(H,H)C(H,H)CH_2), ν(CN)
971	962	967	δ_{oop}(NC(H)C)$_{Py}$(55),δ_{oop}(CC(H)C)$_{Py}$, δ_{oop}(CC(H)N)$_{Py}$, δ_p(Py)
981	979		ν(CC)(45), ρ_r(CCH_3), ρ_r(C_αN(H)C), γ(C_αN(H)C), ρ_b(POH)
986	985	985	δ_{oop}(CC(H)C)$_{Ph}$(80), ρ_b(POH), γ_{as}(Ph)
	986	989	ρ_b(P(OH))(63), δ_{oop}(CC(H)C)$_{Ph}$
	994		δ_{oop}(CC(H)C)$_{Py}$(79), δ_{oop}(CC(H)N)$_{Py}$, δ_p(Py)
996			δ_{trig}(Py)(58), ν(CN)$_{Py}$, ν(CC)$_{Py}$
999	999	1002	δ_{trig}(Ph)(47), ν(CC)$_{Ph}$
1003		999	γ(CC(H)C)$_{Py}$(69), δ_p(Py), δ_{oop}(NC(H)C)$_{Py}$
1004	1005	1005	δ_{oop}(CC(H)C)$_{Ph}$(81), δ_p(Ph)
	1023		δ_{trig}(Py)(41), ν(CC), ν(CC)$_{Py}$
1024	1024		ν(CC)(46), ρ_r(CCH_3), ν(CN), ν(CC), δ_{trig}(Py), ρ_r(CCH_3), ν(CC)$_{Py}$
1030	1031	1028	ν(CC)$_{Ph}$(46), δ_{trig}(Ph), ρ_r(CC(H)C)$_{Ph}$
1048	1045		ν(CC)$_{Py}$(47), ν(C_αN), ν(CC), ρ_r(CC(H)C)$_{Py}$, ρ_b(CC(H)C)$_{Py}$
1057	1053	1077	ν(CC)(33), ν(C_αN), ν(CC)$_{Py}$, ν(CN)$_{Py}$
1079	1080	1081	ν(CC)$_{Ph}$(52), ρ_r(CC(H)C)$_{Ph}$, ρ_b(CC(H)C)$_{Ph}$
1092	1106	1113	ν(CN)(29), ν(C_αN), ν(CC)
1102	1119		ρ_r(CC(H)N)$_{Py}$(20), ν(CC)$_{Py}$, ρ_r(CC(H)C)$_{Py}$, ν(CN), ν(C_αN), ρ_b(CC(H)C)$_{Py}$, ν(CN)$_{Py}$
1109	1109		ν(CC)$_{Ph}$(27), ν(C_{Ph}P), δ_{trig}(Ph), ρ_r(CC(H)C)$_{Ph}$, ρ_b(CC(H)C)$_{Ph}$
1124	1133		ν(CN)(17), ρ_r(CCH_3), ρ_r(C(H,H)C(H,H)CH_2), ρ_r(PC_α(H,C_{Py})N), ν(CN), ρ_r(C(H,H)C(H,H)CH_3), ρ_s(CH_2), ν(CC), ρ_t(C(H,H)C(H,H)CH_2), ρ_r(CC(H,H)C), ρ_s(NC(H,H)C), ν(CC)$_{Py}$, ρ_b(CC(H)C)$_{Py}$
1143	1141		ρ_r(NC(H,H)C)(22), ν(POH), γ(C_αN(H)C), ρ_r(C(H,H)C(H,H)CH_2), ν(C_αN), ρ_r(CC(H,H)C), ν(CC)
1153			ν(POH)(62), ρ_r(PC_α(H,C_{Py})N)
1157			ρ_r(CC(H)N)$_{Py}$(55), ρ_r(CC(H)C)$_{Py}$, ν(CC)$_{Py}$
1164	1165	1166	ρ_r(CC(H)C)$_{Ph}$(74), ν(CC)$_{Ph}$, ρ_b(CC(H)C)$_{Ph}$
1179	1182		ρ_r(PC_α(H,C_{Py})N)(44), ν(POH), ρ_r(C_α(H,C_{Py})N), ν(CC)$_{Py}$, ρ_b(CC(H)C)$_{Py}$

1183	1185	1185	$\rho_r(CC(H)C)_{Ph}(62)$, $\rho_r(PC_\alpha(H,C_{Py})N)$, $\nu(CC)_{Ph}$, $\rho_b(CC(H)C)_{Ph}$, $\rho_r(C_\alpha(H,C_{Py})N)$
1201	1195	1196	$\nu(C_\alpha C_{Py})(23)$, $\rho_r(C_\alpha(H,C_{Py})N)$, $\delta_{trig}(Py)$, $\rho_t(NC(H,H)C)$, $\rho_r(PC_\alpha(H,C_{Py})N)$, $\nu(CC)_{Py}$, $\rho_b(CC(H)C)_{Py}$, $\nu(CN)_{Py}$, $\rho_r(CC(H)N)_{Py}$
	1218	1225	$\nu(PO)(15)$, $\nu(C_\alpha C_{Py})$, $\rho_r(PC_\alpha(H)N)$, $\rho_r(C_\alpha C(H)N)_{Py}$, $\rho_r(CC(H)N)_{Py}$, $\delta_{trig}(Py)$, $\rho_b(CC(H)C)_{Py}$, $\nu(CC)_{Py}$
1230	1235	1237	$\rho_t(CC(H,H)C)(29)$, $\rho_t(NC(H,H)C)$, $\nu(C_\alpha C_{Py})$, $\rho_t(C(H,H)C(H,H)CH_2)$, $\rho_r(CCH_3)$, $\nu(CN)_{Py}$, $\rho_r(C(H,H)C(H,H)CH_3)$, $\rho_r(CC(H,H)C)$
1248	1242		$\nu(PO)(57)$, $\nu(CC)_{Py}$, $\nu(CN)_{Py}$, $\rho_t(C(H,H)C(H,H)CH_2)$, $\rho_r(C_\alpha(H,C_{Py})N)$
1249			$\nu(PO)(39)$, $\nu(CN)_{Py}$, $\rho_t(C(H,H)C(H,H)CH_2)$, $\nu(C_\alpha C_{Py})$
1274	1262		$\nu(CN)_{Py}(38)$, $\nu(CC)_{Py}$, $\rho_r(PC_\alpha(H)N)$, $\nu(PO)$
	1273		$\rho_t(NC(H,H)C)(22)$, $\rho_t(CC(H,H)C)$, $\rho_w(CC(H,H)C)$, $\rho_r(PC_\alpha(H)N)$
1296	1295	1296	$\nu(CC)_{Ph}(80)$, $\rho_r(CC(H)C)_{Ph}$, $\rho_b(CC(H)C)_{Ph}$
1299	1299		$\rho_t(CC(H,H)C)(27)$, $\rho_r(CC(H)N)_{Py}$, $\nu(CN)_{Py}$, $\rho_w(C(H,H)C(H,H)CH_2)$, $\rho_r(CC(H)C)_{Py}$, $\rho_w(C(H,H)C(H,H)CH_3)$, $\rho_r(C_\alpha(H,C_{Py})N)$, $\rho_t(NC(H,H)C)$, $\rho_r(PC_\alpha(H)N)$, $\rho_w(NC(H,H)C)$
1305	1306		$\rho_t(C(H,H)C(H,H)CH_3)(59)$, $\rho_t(C(H,H)C(H,H)CH_2)$, $\rho_t(NC(H,H)C)$, $\rho_w(C(H,H)C(H,H)CH_2)$, $\rho_w(CC(H,H)C)$, $\rho_r(PC_\alpha(H)N)$, $\rho_t(CC(H,H)C)$, $\rho_r(C_\alpha(C_{Py},H)N)$
1313	1316		$\rho_w(CC(H,H)C)(37)$, $\rho_t(CC(H,H)C)$, $\rho_t(NC(H,H)C)$, $\rho_w(C(H,H)C(H,H)CH_3)$, $\rho_w(C(H,H)C(H,H)CH_2)$, $\rho_t(C(H,H)C(H,H)CH_3)$, $\rho_r(CC(H)N)_{Py}$, $\rho_w(NC(H,H)C)$, $\rho_r(C_\alpha(H,C_{Py})N)$
1326	1328	1329	$\rho_r(CC(H)C)_{Ph}(58)$, $\nu(CC)_{Ph}$
1372	1369		$\rho_w(CC(H,H)C)(58)$, $\rho_w(C(H,H)C(H,H)CH_2)$, $\rho_w(C(H,H)C(H,H)CH_3)$, $\nu(CC)$, $\rho_w(NC(H,H)C)$
1378	1379	1369	$\rho_w(NC(H,H)C)(67)$, $\rho_r(C_\alpha(H,C_{Py})N)$, $\rho_w(C(H,H)C(H,H)CH_3)$, $\rho_w(CC(H,H)C)$
1386	1386		$\delta_s(CCH_3)(90)$
1439	1431	1419	$\rho_r(CC(H)N)_{Py}(51)$, $\nu(CC)_{Py}$
1445	1444	1445	$\rho_r(CC(H)C)_{Ph}(58)$, $\nu(CC)_{Ph}$, $\rho_b(CC(H)C)_{Ph}$
1447	1445		$\rho_s(CC(H,H)C)(82)$, $\rho_s(CC(H,H)C)$, $\rho_s(C(H,H)C(H,H)CH_2)$, $\rho_s(C(H,H)C(H,H)CH_3)$
1462	1462		$\rho_s(C(H,H)C(H,H)CH_3)(47)$, $\delta_{as}(CH_3)$, $\rho_s(C(H,H)C(H,H)CH_2)$, $\rho_s(CC(H,H)C)$, $\rho_r(CH_3)$
1469	1469		$\delta_{as}(CH_3)(70)$, $\rho_r(CCH_3)$, $\rho_r(CH_3)$, $\rho_r(C_\alpha N(H)C)$
1474	1476		$\rho_s(CH_2)(66)$, $\delta_{as}(CH_3)$, $\rho_s(CC(H,H)C)$, $\rho_r(CH_3)$
1477	1476		$\rho_r(CH_3)(47)$, $\delta_{as}(CH_3)$, $\rho_s(C(H,H)C(H,H)CH_3)$, $\rho_s(CH_2)$,
			$\rho_s(CC(H,H)C)$
1480	1484		$\rho_r(CC(H)N)_{Py}(24)$, $\rho_r(CC(H)C)_{Py}$, $\nu(CN)_{Py}$, $\rho_s(NC(H,H)C)$, $\rho_r(C_\alpha C(H)N)_{Py}$, $\rho_b(CC(H)C)_{Py}$, $\nu(CC)_{Py}$
1489	1490	1490	$\rho_r(CC(H)C)_{Ph}(65)$, $\nu(CC)_{Ph}$
1490	1486	1480	$\rho_r(C_\alpha N(H)C)(76)$, $\rho_s(NC(H,H)C)$
1585	1580	1574	$\nu(CC)_{Py}(53)$, $\nu(CN)_{Py}$, $\rho_r(CC(H)N)_{Py}$, $\delta_{as}(Py)$
1588	1587	1587	$\nu(CC)_{Ph}(68)$, $\rho_r(CC(H)C)_{Ph}$, $\delta_{as}(Ph)$
1602	1601	1604	$\nu(CC)_{Py}(52)$, $\nu(CN)_{Py}$, $\delta_{as}(Py)$, $\rho_r(CC(H)C)_{Py}$, $\rho_r(CC(H)N)_{Py}$, $\rho_b(CC(H)C)_{Py}$, $\rho_r(C_\alpha C(H)N)_{Py}$
1604	1604	1604	$\nu(CC)_{Ph}(61)$, $\delta_{as}(Ph)$, $\rho_r(CC(H)C)_{Ph}$, $\rho_b(CC(H)C)_{Ph}$
	2844		$\nu(CH)(99)$
2909	2900		$\nu(C_\alpha H)(99)$, $\nu(CH)$
2952	2947	2933	$\nu(CH)(96)$
2960	2957		$\nu(CH)(94)$
2966	2966		$\nu(CH)(95)$
2976	2973		$\nu(CH)(98)$
2986			$\nu(CH)(85)$
2997			$\nu(C_\alpha H)(95)$
2998	3001	3012	$\nu(CH)(90)$
3026	3026		$\nu(CH)(97)$
3032	3031		$\nu(CH)(99)$
	3035		$\nu(CH)(98)$
3094	3088	3088	$\nu(CH)_{Py}(99)$
3105	3105	3104	$\nu(CH)_{Ph}(93)$
3112	3108		$\nu(CH)_{Py}(97)$
3116	3114	3114	$\nu(CH)_{Ph}(98)$
	3116	3119	$\nu(CH)_{Py}(98)$
3125	3123	3125	$\nu(CH)_{Ph}(97)$
3126	3131		$\nu(CH)_{Py}(98)$
3133	3131	3133	$\nu(CH)_{Ph}(98)$
3138	3138	3140	$\nu(CH)_{Ph}(96)$
3138		3148	$\nu(CH)_{Py}(96)$
3411			$\nu(OH)(56)$, $\nu(NH)$
3424			$\nu(NH)(56)$, $\nu(OH)$
	3479	3462	$\nu(NH)(100)$
	3751	3741	$\nu(OH)(100)$

Abbreviations: ν, stretching; δ, deformation; γ, torsion; δ_{trig}, trigonal deformation; δ_p, puckering; ρ_b, bending; ρ_r, rocking; ρ_t, twisting; ρ_w, wagging; ρ_s, scissoring; as, asymmetric; oop, out of plane; Py, pyridine ring; Ph, phenyl ring; C_α, an asymmetric carbon atom