Supporting Information

Bifacial Raman Enhancement on Monolayer Two-dimensional Materials

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Table S1. Enhancement Factors of Different Raman Modes of CuPc on Different Substrates

$\omega_{exp}(cm^{-1})$	$\omega_{the}(cm^{-1})$	EF $_{G,SL}$	EF $_{G,DL}$	EF $_{BN,SL}$	EF $_{BN,DL}$	$Ratio_G$	$Ratio_{BN}$	Mode assignment
682	675	3.1	5.1	5.2	8.9	1.6	1.7	Macrocycle breathing, most contributed by the change of C-N and C-C bond angle
749	748	7.6	13.5	9.4	16.0	1.8	1.7	Pyrrole out of plane bending
1109	1115	3.4	6.4	4.3	7.1	1.9	1.7	C-H and Cu-N bending
1144	1155	11.7	26.5	30.5	40.7	2.3	1.3	C-H deformation and outer ring breathing
1306	1300	4.5	9.5	6.0	8.2	2.1	1.3	Cu-N asymmetric stretching and C-N stretching
1341	1334	10.7	22.5	30.8	38.9	2.1	1.3	Cu-N symmetric stretching and C-N stretching
1452	1462	8.0	16.3	8.6	13.8	2.0	1.6	benzene ring C-C stretching
1531	1548	26.6	47.9	28.5	39.5	1.8	1.4	C=N and C=C stretching

ω_{exp} and ω_{the} are the experimental and calculated Raman shift of CuPc molecule, respectively. EF$_{G,SL}$ and EF$_{BN,SL}$ are the enhancement factors of vibration modes of single-layer (SL) CuPc molecules on graphene and h-BN, respectively. EF$_{G,DL}$ and EF$_{BN,DL}$ are the enhancement factors of vibration modes of double-layer (DL) CuPc molecules on graphene and h-BN, respectively. $Ratio_G$ and $Ratio_{BN}$ are the ratios of Raman signal of double-layer of molecules versus single-layer ones, respectively. The vibrational modes are assigned by Gaussian 03 package.
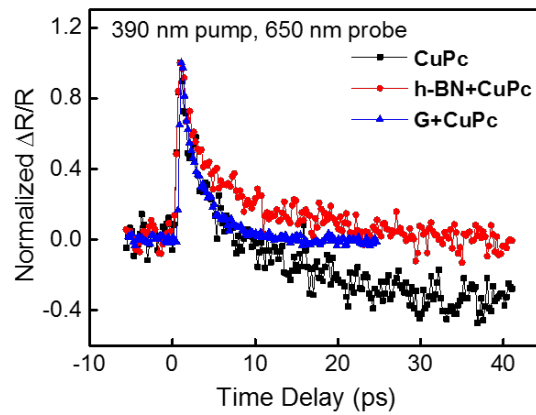

Figure S1. Measured reflectivity for three samples of CuPc on blank 300 nm SiO$_2$/Si (black line), h-BN (red line) and graphene (blue line).
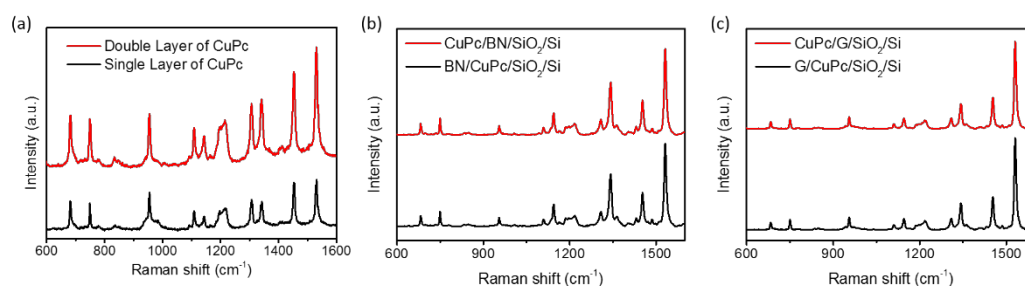
Figure S2. Raman spectra of double-layer CuPc molecules and single-layer CuPc molecules on blank SiO$_2$/ Si (a). Comparison of Raman spectra of CuPc molecules on and underneath *h*-BN (b) and graphene (c).

The intensity of double-layer CuPc molecules on SiO$_2$/Si was twice that of single-layer CuPc, as shown in Figure S2a. Figure S2b and S2c show that the intensities were almost the same when the molecules were under and on the top of the 2D material. Only a difference of less than 4% was observed. The relative intensities of the Raman peaks were also the same for molecules on the top and under 2D materials.

To make sure that the amount of deposited molecules is equal on both blank SiO$_2$/Si region and 2D materials, XPS (X-ray photoelectron spectroscopy) measurements were carried out, and the full XPS spectra were as shown in Figure S3a. The intensities of Cu 2p3/2 peak at around 950 eV on SiO$_2$/Si and graphene regions were almost the same (Figure S3b), while the intensity of C 1s peak at around 285 eV on SiO$_2$/Si region was nearly half of that on graphene region for the contribution of the carbon from graphene (Figure S3c). The results indicated that the 2D materials would not change the amount of deposited CuPc molecules.
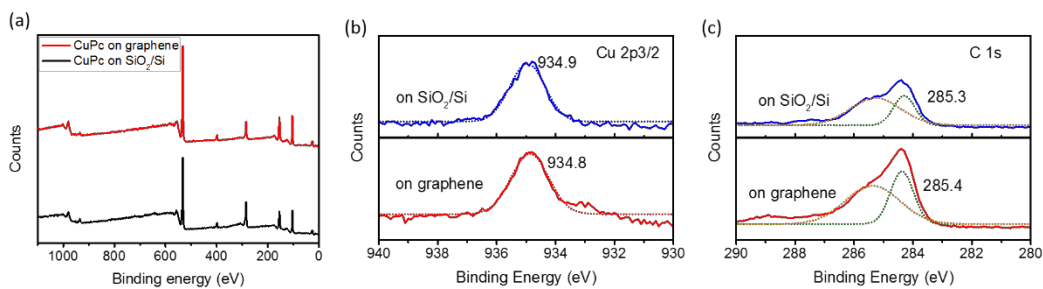
Figure S3. The XPS scanning spectra of CuPc on blank SiO_2/Si (black) and graphene (red). Well-resolved XPS spectra of Cu 2p3/2 (b) and C1s (c) of CuPc molecules on blank SiO_2/Si (blue) and graphene substrate (red).

Table S2 Calculated Total Energies of CuPc/BN under different adsorption configurations(eV)

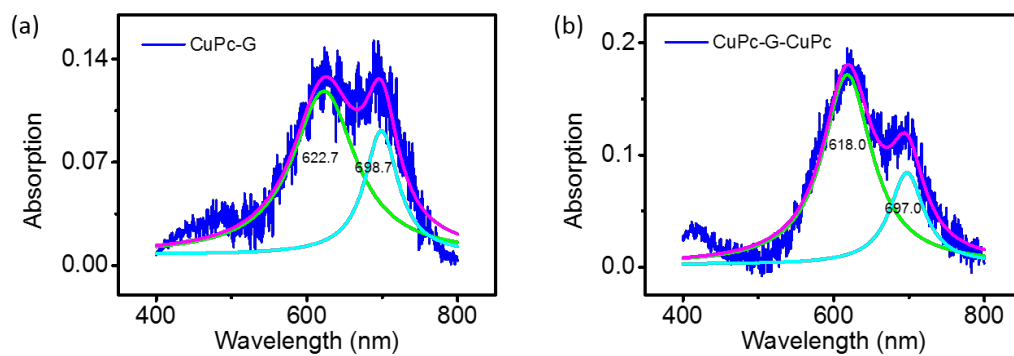| Rotation / Translation	$0°$	$15°$	$30°$	$45°$	$60°$
Cu on Nitrogen	-2946.60	-2946.50	-2946.61	-2946.50	-2946.60
Cu on Boron	-2946.51	-2946.60	-2946.53	-2946.60	-2946.52

Figure S4. Comparison of the absorption spectra of CuPc molecules on one surface (a) and on both surfaces of a monolayer graphene flake (b).
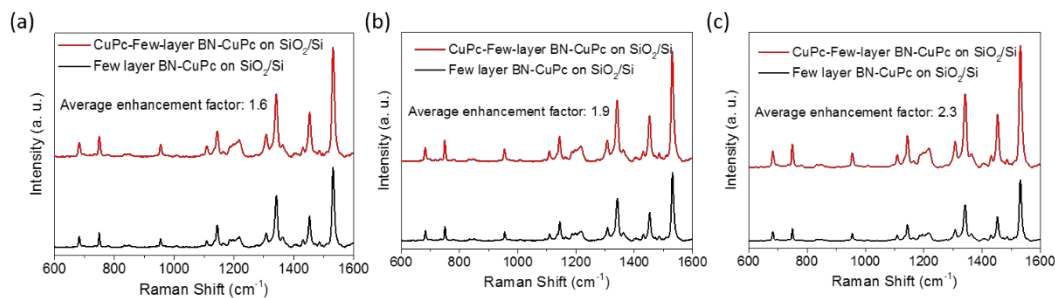
Figure S5. Raman spectra of double-layer CuPc molecules and single-layer CuPc molecules enhanced by *h*-BN of different thickness: 2.7nm (a), 4.6 nm (b) and 6.4 nm (c), respectively.
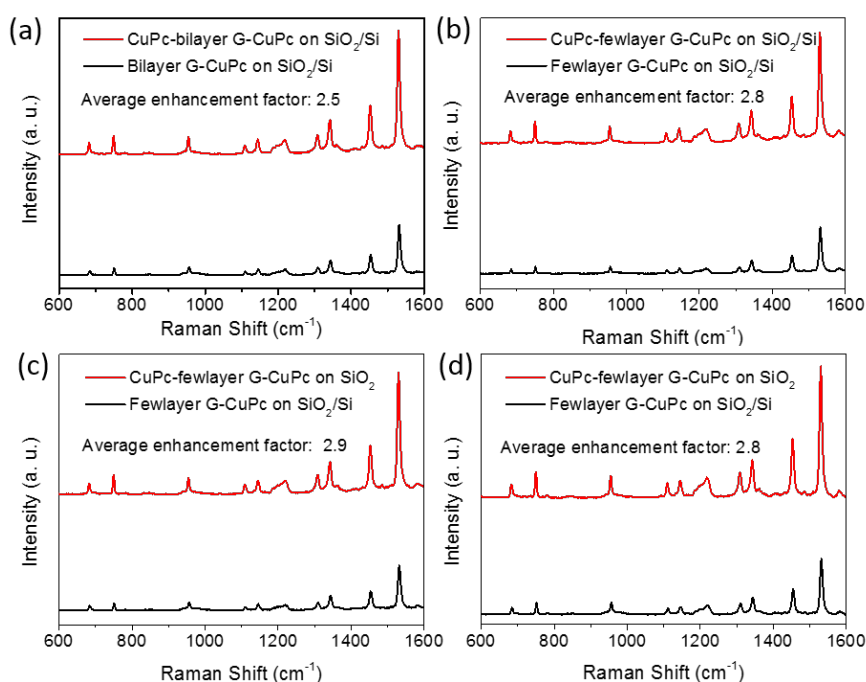

Figure S6. The Raman spectra of double-layer CuPc molecules and single-layer CuPc molecules enhanced by graphene of different thickness: 1.7 nm (a), 2.7 nm (b), 3.4 nm (c) and 5.5 nm (d), respectively.

The surface coverage of deposited CuPc molecules can be estimated as follows. During deposition, the thickness is monitored by the frequency change of the quartz monitor crystals. Since CuPc was not a material in the program for monitoring the thickness, carbon (graphite, $\rho_M = 2.25 \ g/cm^3$) was chosen instead. The defined thickness of deposition in our experiment was 3 Å. The increased mass of the deposited material is:

$$\Delta m = A * \rho_g * \Delta d_g = M_{CuPc} * n_{CuPc}/N_A$$

where A is the deposition area of the sample, ρ_g is the density of the graphite film, Δd_g is the thickness change of graphite, M_{CuPc} is the relative molar mass of CuPc, n_{CuPc} is the number of CuPc molecules, and N_A is Avogadro's constant. Then the number of deposited CuPc molecules is:

$$n_{CuPc} = \frac{A * \rho_g * \Delta d_g * N_A}{M_{CuPc}}$$

and the area of CuPc (A_{CuPc}) of the same mass as graphite can be calculated by:

$$A_{CuPc} = A_{CuPc\_single} * n_{CuPc}$$

where A_{CuPc_single} is the area of a single CuPc molecule deposited on silica.

The degree of surface coverage (sc) of CuPc on the sample can be calculated by:

$$sc = \frac{A_{CuPc}}{A} = \frac{A_{CuPc\_single} * n_{CuPc}}{A} = \frac{A_{CuPc\_single} * \rho_g * \Delta d_g * N_A}{M_{CuPc}}$$

where the value of A_{CuPc_single} is adopted as that on TiO$_2$(110) surface, which is around 2 nm^2 [S1]. $M_{CuPc} = 576.08 \; g \cdot mol^{-1}$, $N_A = 6.02 \times 10^{23}$ mol^{-1}. Then

$$sc = \frac{2 \; nm^2 * 2.25 \; g \cdot cm^{-3} * 3\text{Å} * 6.02 * 10^{23} mol^{-1}}{576.08 \; g \cdot mol^{-1}} \approx 1.4$$

So the surface coverage is estimated to be ~1.4 in an ideal situation with all molecules in monomeric state. Assumed that half of the molecules are in aggregated state of tetramer in π-π stacking and the other half in monomeric state, then the surface coverage is 0.88. In this regard, the density of molecules is sufficent for the overlapping in 2D material's plane on the two surface.

References:
S1. Wang, Y.*; Wu, K.*, Kröger, J.; Berndt, R. Structures of Phthalocyanine Molecules on Surfaces Studied by STM. *AIP Adv.,* **2012**, *2*, 041402.