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Excited state charge transfer promoted Raman enhancement of copper phthalocyanine by twisted bilayer graphenes



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ABSTRACT

Few atom thick, twisted bilayer graphene (tBLG) possesses a rotation angle (θ) dependent van Hove singularity (vHs). Fine-tuning vHs serves a potential method to enhance charge transfer (CT) in surface enhanced Raman spectroscopy. This study shows that tBLG having a specific θ promotes as high as a 1.7 times enhancement of the Raman signals of copper phthalocyanine (CuPc) as compared to that caused by single layer graphene (SLG). The results of a combination of reflection imaging spectroscopy and widefield Raman provide spatial and spectral information about both tBLG with θ ranging from 10.9 to 13.7° and the corresponding vHs. Comparison of Raman spectra of CuPc in presence and absence of tBLG demonstrates that a significant enhancement of certain CuPc vibrational modes occurs when the underlying tBLG possesses a $\theta = 12.2^\circ$, showing as high as 6.8 and 1.7 times enhancements of certain vibrational mode as compared to those of CuPc on bare and SLG substrates, respectively. Theoretical calculations indicate that a match between the energies of vHs of tBLG with those of frontier orbitals of CuPc facilitates CT from the distant SLG to CuPc.

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1. Introduction

Since the discovery of Raman signal enhancement of pyridine on silver electrodes, surface enhanced Raman scattering (SERS) has drawn enormous attention owing to the unique opportunity it provides for detecting infinitesimal amounts of analytes [1]. SERS takes place through both electromagnetic (EM) and chemical (CM) mechanisms [2]. The EM component of SERS, caused by a locally intensified electrical field in resonance with surface plasmon wavelength of noble metals, results in an enhancement factor (EF) reaching 10⁸ or more [3]. In contrast, CM results from either charge transfer (CT) or dipole-dipole interactions with the underlying substrate and it causes a lower Raman EF as compared to that promoted by EM [4–6]. Despite being striking large, EF induced by EM varies with local hot spots exists between rough metal surfaces. As a result, control over the reproducibility and uniformity [3] of EF is a major issue being actively pursued in efforts aimed at furthering the use of SERS for analyte detection.

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Graphene enhanced Raman scattering (GERS) has received attention owing to the fact that CM can be optimized because of the seamless atomic flat surface and chemical inertness of graphene [7–13]. The intrinsic plasmon of single layer graphene (SLG), existing at a few hundred micrometers in association with the band gap of semimetallic graphene, is negligibly effected by EM in the visible range [8]. Therefore, unlike noble metals graphene exerts CM in the visible light range [9]. Thus far, GERS has been observed to exert a greater enhancement of Raman signals displayed by molecules with planar structures (i.e., phthalocyanine (Pc) [7], copper/zinc phthalocyanine (Cu/ZnPc) [9–13], porphyrin [7,10,12], and perflourinated CuPc [6]) than those with nonplanar structures [11]. This phenomenon is a result of a 'structural factor' which enables intimate π - π interactions between the analytes and graphene [11]. Most studies aimed at enhancing GERS have focused on varying the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of molecules [11], the number of graphene layers [12], the Fermi level of graphene by doping, and the phonon energy [11]. A less well-explored question is how control of the electronic structure of graphene can be utilized to enhance and modulate the EF of GERS.

Twisted bilayer graphene (tBLG), formed by stacking of SLGs with a fixed rotational angle (θ) (Fig. 1C) [14–19], possesses a large



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Fig. 1. Raman enhancement of CuPc depending on the rotation angle (θ) of tBLG which modulates vHs. (A) Schematic of CuPc on a tBLG lattice. (B) Energies associated with the HOMO and LUMO of CuPc, and DOS of tBLG, and excited-state and ground-state CT from vHs to frontier orbitals of CuPc. Left arrows against *y* axis indicate Stokes Raman processes occurring at CuPc upon photoexcitation. Right arrows in DOS of tBLG allowed transitions at vHs. (C) tBLG structure with θ indicated. (A colour version of this figure can be viewed online.)

superlattice structure known as a Moire superlattice. Unlike Bernalstacked BLG (bBLG), tBLG displays van Hove singularity (vHs) transitions (E_{vHs} , blue arrows in Fig. 1B), on top of a density of states (DOS, red curve in Fig. 1B) that are similar to those in bBLG. The optoelectronic properties of tBLG can be tuned by controlling θ (Fig. 1C) to suit various fundamental research objectives such as superconductivity [17], Hofstadter's butterfly [20] and chiral twodimensional (2D) materials [16]. Superconductivity of tBLG was found to occur only at specific θ values (*ca*. 1°) [17], suggesting that adjusting θ of tBLG and other two-dimensional materials possibly provides an approach for obtaining interesting properties. Along this line, when $E_{\rm vHs}$ of tBLG is in resonance with excitation laser, a larger Raman G band enhancement with 10-100 is produced [21,22]. Moreover, tBLG with electron donating nature is reactive via the CT with benzene diazonium salt derivatives with rates that vary with the E_{vHs} of the tBLG [23,24]. These observations indicate that by controlling the vHs it might be is possible to utilize tBLG to enhance CT.

In the study described below, we investigated changes taking place in the Raman signal of CuPc on tBLG upon varying the rotation angle of the tBLG. In these experiments, chemical vapor deposition (CVD)-grown tBLG was utilized to serve as a Raman enhancement substrate for CuPc. A combination of optical spectroscopy techniques, including reflection imaging spectroscopy (RIS) and wide-field Raman spectroscopy (WFR), was used to gain spatial and spectral information about the tBLG both before and after near monolayer CuPc deposition. EF of CuPc on tBLG substrate was assessed as a function of θ . The peculiarly large EF of CuPc/tBLG at a specific θ was investigated by using density functional theory (DFT), which show that state mixing between the furthest graphene layer in tBLG and frontier orbitals of CuPc is enhanced at a θ value near 12.2°.

2. Results and discussion

tBLG, used as a GERS substrate for CuPc, was obtained by growing on a Cu foil using the CVD method and by slowly feeding the carbon feedstock. Briefly, as-received Cu foil was used as both substrate and catalyst to grow graphene by flowing 5 standard cubic centimeter per min (sccm) methane, 10 sccm Ar and 100 sccm H₂ over a hot zone at 950 °C for 12 h duration under reduced pressure (*i.e.*, 30 mTorr) [25–27]. After cooling to room temperature, poly (methyl methacrylate) (PMMA) was spincoated on the graphene/Cu substrate as a protective layer before etching away the underlying Cu foil and transferring to a 285 nm-thick SiO₂/Si substrate. Subsequently, the PMMA layer was removed by prolonged exposure to hot acetone vapor.

The formation of tBLG and subsequent determination of θ were

initially investigated by using RIS, in which a reflected light spectrum in a specific spatial position is generated by obtaining a series of reflection images synchronized with each excitation wavelength (λ) . This method is like absorption spectroscopy in that it yields spatial and spectral information about the tBLG over the visible range [15,27]. Fig. 2A depicts schematic of the RIS instrument, which consists of a broadband Xe lamp, subtractive double monochromators and a convex lens in the sample chamber before an upright microscope equipped with charge coupled device (CCD) detector. Note that widefield rather than focused illumination of graphene sample (circled image in Fig. 2A), an essential feature of the method, is created by using a convex lens whose focal length corresponds the length to back focal plane of objective lens (see Fig. S1 for schematics). Fig. 2B shows an optical image (OM) of a representative graphene generated using RIS under white light illumination. SLG, BLG and few layered graphene (FLG) on the 285 nm-thick SiO₂/Si substrate are clearly discernible as contrast differences in the image [28]. In using RIS in a spectral mode, the CCD detector collects stacks of widefield-illuminated images created by excitation over the 440–650 nm range. The image movie shown in Smovie1 reveals the spatial position of not only graphene analogues, but also of PMMA residues and graphene wrinkles, which enable exclusion of artifact effects and location of previously interrogated positions. Unlike monotonous changes of brightness that are present in SLG and bare substrate areas, tBLG containing regions exhibit transition-like reflection changes that vary according to λ , indicating the existence of E_{vHs} of tBLG (right panel of Fig. 1B). Fig. 2C is the combined image of these tBLG domains, created by overlaying a pair of original images and the λ -corresponding color (*i.e.*, green for 540 nm), and then stacking to form a single image using Image[[29] program like RGB color mixing. Inspection of the image shows that the dotted enclosed areas near the FLGs boundaries exhibit different colors (*i.e.*, blue and green). indicating the existence of tBLG vHs [27]. Optical spectra of the tBLGs were obtained by setting each frame as a corresponding λ and brightness as reflection intensity in a given area [30]. Net reflection spectra (Rnet) from tBLG domains were obtained by subtracting the reflection signal of bBLG (R_{bBLG}/R_{sub}) from the reflection of tBLG ($\Delta R_{\text{tBLG}}/R_{\text{sub}}$) using the equation R_{net} = $(\Delta R_{\text{tBLG}} - \Delta R_{\text{bBLG}})/R_{\text{sub}}$, in which R_{sub} is the reflection spectrum from a blank substrate. Representative R_{net} spectra recorded on various tBLG domains from various samples (Fig. 2D) consist of large reflection signals originating from E_{vHs} followed by slight dips at lower energy, which arise from anticrossing of band structures, as shown in Fig. 1B [31]. Moreover, spectrum shapes of tBLG resembles exciton-derived Fano shape and are in good agreement with the literature [32,33]. In this manner, various $E_{\rm vHs}$ of tBLG were obtained in the 2.00–2.52 eV range. Furthermore, the $E_{\rm vHs}$ values



Fig. 2. Spatial and spectral determination of tBLGs with θ_{vHs} by using RIS. (A) Schematic of the RIS instrument. Enclosed schematic illustrates widefield illumination of excitation light *via* objective lens on a graphene sample. (B) OM image of the grown FLGs on a 285-nm thick SiO₂/Si substrate. Dashed enclosures indicate tBLG domains. (C) Composite reflection image of FLGs with matching color codes corresponding to E_{vHs} . Closer inspection of dashed enclosures shows green and blue colors from tBLG at different θ_{vHs} . White color originates from multilayer graphene possessing large reflection values over the entire visible range. θ_{vHs} in legend determined using equation 1. (D) Representative R_{net} spectra of tBLGs having various E_{vHs} . (A colour version of this figure can be viewed online.)

were used to calculate vHs-based rotation angles (θ_{vHs}) using equation (1) [22],

$$E_{\rm vHs} = E_{\rm o} |\sin \left(3\theta_{\rm vHs} \right)| \tag{1}$$

where E_0 is 3.9 eV. By utilizing data from 15 different tBLG samples, the θ_{vHs} were found to be in the range of 10.9–13.7°.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.carbon.2021.11.070.

Confirmatory information about the nature of the tBLG was obtained by using atomic force microscopy (AFM). Figs. S2A and S2B shows respective OM and RIS derived images of graphene regions. A comparison of these images enables identification of distinct tBLG regions. The AFM height image (Fig. S2C) of this region shows the topography of tBLG, along with residual PMMA speckles and graphene wrinkles having heights of a few tens of nanometer which originate from shrinkage of graphene during cooling in the CVD process caused by the thermal expansion coefficient difference between graphene and Cu [34]. A comparison of the bottom regions of tBLG and SLG (Fig. S2D) yields a height difference of 0.37 nm which corresponds to monolayer graphene. This measurement enables verification of the layer number of graphenes.

Another approach to assessing the θ value utilizes Raman spectroscopy to measure rotational (R) bands, which are associated with intervalley transverse-optical (TO) resonance between *K* and *K* points in the Brillouine zone of tBLG [35,36] (see inset of Fig. S3 for phonon process). The frequency of the R band is inversely related to θ (Fig. S3) [22,37]. Especially, R bands are associated with tBLG having θ greater than 10°. R band spectra of spatially

distributed tBLG regions were located and analyzed by using WFR, a Raman technique [6,27,38,39] that also utilizes global illumination by a laser through a convex lens like that employed in RIS. In the image mode, a bandpass filter is placed in the emission side to image specific frequency bands, such as G and 2D bands of graphene. In a spectral mode, the instrument is used to measure the line spectrum from the center position of the image mode which contains a streak of respective band [15,27]. Fig. 3A shows an OM image of the graphene region. Although tBLG regions are barely visible in the OM image, the corresponding G band image (left panel in Fig. 3B) contains bright regions originating from G band enhancement of tBLG [27]. Inspection of spectra containing G and 2D bands (middle and right panels in Fig. 3B, respectively), obtained using the line spectrum mode, shows that Raman shift and intensity variations exist in intensity along z axis. As can be seen by viewing Fig. 3C, a R band near 1480 cm⁻¹ appears next to the intense G band from tBLG. Because of its dependence on the rotation angle by employing the literature method (Fig. S3), the R band position (ω_R) in Fig. 3D was utilized to determine θ (θ_R) [22,37]. ω_R progressively upshifted as increasing $\theta_{\rm R}$. The $\theta_{\rm R}$ values of 14 different tBLG grains were also obtained using this technique (Table S1) and utilized to produce θ obtained as averages of $\theta_{\rm R}$ and θ_{vHs} (*i.e.*, OM image, G band image, RIS image, domain size, R band position, θ_{R} , E_{vHs} , θ_{vHs} , and θ). The domain size of tBLG with various θ varies from 12 to 196 μ m² in which the smallest domain provides at least 15 different Raman spectrum pixels in line spectra to be averaged considering the magnification and pixel size of the spectral CCD. The average difference between $\theta_{\rm R}$ and $\theta_{\rm vHs}$ of 15 different grains was found to be 0.26° ranging from -0.02° up to



Fig. 3. Determination of θ_R by using WFR and line Raman spectroscopy. (A) OM image of tBLG-containing area. (B) Corresponding WFR of G-band from tBLG regions generated using an imaging mode (left), and subsequent Raman spectra near G band (middle) and 2D band (right) from red dashed line generated using a spectral mode. Yellow dashed lines are drawn to indicate grain boundaries for visual comparison of the image and spectra. (C) Representative Raman spectra of tBLG containing R band from line Raman spectra. (D) Changes of R band position according to tBLG and R band-based determination of θ_R . (A colour version of this figure can be viewed online.)

 0.62° , which supports the reliability of the two methods for determining θ . However, upon closer look of Table S1, there is a tendency that θ_{vHs} is in general underestimated than θ_R . It probably originates from the fact that RIS spectrum contains contributions from excitonic effect [32,33] which slightly lowers E_{vHs} and is not considered in equation (1).

After characterizations of various tBLG regions and determination of the corresponding θ values, CuPc deposition was carried out. In this process, it is important to create a uniform monolayer thick CuPc layer because higher layers of this material exhibit lower EF owing to the first layer effect of GERS [10,40], in which enhancement mediated by CT decreases as the distance between the graphene and the molecule increases. Uniform CuPc deposition on a tBLG containing substrate was achieved by using vacuum thermal evaporation (see Experimental). The thickness and topography of the layers were monitored using a quartz microbalance in situ and AFM ex situ. The height topography (Fig. 4A) determined for the interfacial region between the deposited and bare areas on SiO₂/Si subtrate created during thermal evaporation revealed that the average thickness of CuPc (Fig. 4B) is about 0.53 nm, which is about 1.5 times larger than that (*i.e.*, 0.34 nm) of a CuPc monolayer [41]. The gradient thickness originates from a shadow area boundary

created by a metal clip to hold the sample as upside-down manner in a thermal evaporation chamber. Noisy topography seems to originate from adsorption/desorption of small CuPc on native oxide-covered Si cantilever to SiO₂ surface. Raman spectra of the deposited CuPc on SiO₂/Si subtrate (Fig. 4C) contain three major bands at 1342, 1452 and 1530 cm⁻¹, which match the respective literature values of 1344, 1453 and 1530 cm⁻¹) [42]. The vibrational origin of these bands was assigned by using Raman frequency calculations on CuPc with DFT at the B3LYP/6-31G* level as described elsewhere [43]. The vibrational modes depicted as colorcoded CuPc molecules in insets of Fig. 4C are comprised of a most intense $A_{1g}\ band$ at 1530 \mbox{cm}^{-1} (green) resulting from non-metal N–C stretching of the porphyrin group, a B_{2g} band at 1452 cm⁻¹ (orange) corresponding to stretching of the benzene ring, and another A_{1g} band at 1342 cm⁻¹ arising from in-plane symmetric N-C and C-C streching. These assignments are in good agreement with those reported previously [21,43,44]. The Raman spectra recorded for several spots are highly similar, showing intensity variations that are less than 7% and indicating a homogeneous deposition of CuPc. Notably, the intensity of A_{1g} band at 1530 cm⁻¹ of CuPc on a SLG/substrate (Fig. 4D) is about four times higher than that of CuPc alone, indicating that SLG exerts a GERS effect, as was



Fig. 4. Characterization of thermally-deposited CuPc on substrate. (A) AFM height image acquired from the interfacial area between bare and CuPc deposited areas on SiO₂/Si substrate. (B) Height profile near the interface. (C) Offset Raman spectra acquired from 7 different positions on the deposited CuPc. Excitation wavelength: 532 nm. Respective vibrational mode of each band are depicted as insets. (D) Raman spectra of CuPc in presence (top)/absence (bottom) of SLG, normalized by using the Si peak at 520.89 cm⁻¹ as a standard. (A colour version of this figure can be viewed online.)

indicated in an earlier report [7]. The other A_{1g} mode and B_{2g} mode display 1.9 and 1.8 times higher intensities, respectively, than those arising from bare CuPc.

The intimate contact between CuPc and graphene futher prompts to investigate possible CT interaction originating from electronic structure difference. Especially, Raman spectroscopy is a sensitive tool to probe doping and strain of graphene in terms of vibrational shift in G and 2D bands [45-48]. Although direct interrogation into tBLG is desirable, θ -dependent positions of G and 2D from tBLG [22] prompts us to probe SLG instead. For this, comparison of G band position (ω_{G}) and 2D band position (ω_{2D}) of SLG on a SiO₂/Si substrate in absence and presence of CuPc are compared as shown in Raman spectra of Figs. S4A and B, respectively. Comparison of those points were obtained by mapping those Raman bands in doping and strain coordinates which was adapted from the literature (see SI for detailed explanation) [45]. In Fig. S4C, initial SLG sample has similar average (ω_{G} , ω_{2D}) = (1593, 2679) as compared to those (1591, 2679) of SLG [26]. However, CuPc/SLG sample displayed average ($\omega_{\rm G}$, $\omega_{\rm 2D}$) = (1588, 2694) in which $\omega_{\rm G}$ (ω_{2D}) is downshifted (upshifted) as compared to those of the initial SLG. This result suggests that slight *n*-doping and tensile strain occurs after CuPc deposition. Clearly, n-doping of SLG in CuPc/SLG occurs owing to CT. The possible origin of tensile strain from CuPc/ SLG sample is an extended configuration of SLG due to π - π interaction with CuPc and simultaneous decoupled interaction with substrate.

The next stage of this effort focused on determining how EF of CuPc varies according to the θ values of the underlying tBLG. For this purpose, samples described in Fig. 3 and Table S1 were probed using WFR after being subjected to CuPc deposition. Viewing the

WFR derived G band image (Fig. 5A) shows that a large number of bright scattering regions associated with CuPc exist on top of graphene, and that bare locations do not display any scattering. This observation suggests that graphene acts as Raman enhancement substrate. A comparison of Raman spectra of CuPc on tBLG having $\theta = 12.2^{\circ}$, CuPc on SLG, and bare SiO₂/Si substrate (Fig. 5B) shows that tBLG enhances the CuPc bands. Among several with θ values ranging from 10.9° to 13.7° (Fig. 5C), the tBLG with $\theta = 12.2^{\circ}$ enhances formation of the most intense CuPc bands with an ca. 6.8 EF. This result indicates that modulation of θ in tBLG affects EF of CuPc vibrational modes. The EF are slightly different for each vibrational mode, being especially larger for A_{1g} modes than for the B_{2g} (Fig. 5D). The A_{1g} mode at 1530 cm⁻¹, corresponding to non-metal N–C stretching of the porphyrin group, is greatly enhanced by as large as 6.8 times as compared to bare CuPc. In addition, the A_{1g} mode at 1342 cm⁻¹, corresponding to in-plane symmetric N–C and C-C streching, is enhanced by as large as 4.2 times. Finally, the smallest EF (3.3 times) is observed for the B_{2g} mode at 1452 cm⁻¹, which originates from stretching of the benzene ring. Moreover, a comparison of each mode for CuPc on SLG vs tBLG shows that tBLG exhibit a higher EF except for the material with $\theta = 10.9^{\circ}$. In addition, tBLG with $\theta = 12.2^{\circ}$ display 1.7, 2.0, and 2.2 EFs for A_{1g} mode at 1530 $\mbox{cm}^{-1}\!,~B_{2g}$ mode, and A_{1g} mode at 1342 $\mbox{cm}^{-1}\!$ respectively, as compared to those derived from SLG. In addition, the reported finding that FLG causes a similar or inferior EF of vibrational modes from Pc as compared to SLG showing 2-17 EF [7,12] suggests that tBLG with specific θ values has a unique effect on Raman enhancement of CuPc. In fact, CuPC on bBLG has smaller EF as compared to those on SLG. If one considers slightly larger average thickness (0.53 Å) of CuPc than that from that (0.34 Å) of



Fig. 5. GERS effect on CuPc of tBLG with different θ values. (A) G band image of CuPc/tBLG/SiO₂/Si substrate obtained by using WFR. (B) Representative Raman spectra of CuPc/tBLG with $\theta = 12.2^{\circ}$, CuPc/SLG, and CuPc on SiO₂/Si substrate. (C) Intensity changes of CuPc on tBLG with different θ ranging from 10.9 to 13.7°. Each spectra was normalized by using the Si peak at 520.89 cm⁻¹ as the standard. (D) EF comparison of three vibrational modes of CuPc on tBLG with different θ . Shaded lines were drawn to indicate CuPc EF from SLG (circle) and bBLG (triangle) with error. Error bars in x and y axis are generated from the deviation from θ_R and θ_{VHs} and standard deviation from averaging line Raman spectra of each band, respectively. (E) Energy diagram of CuPc on tBLG with $\theta = 12.2^{\circ}$. ES-CT and GS-CT denote excited state- and ground-state CTs, respectively. Bold lines with numbers indicate facilitated transition processes. (A colour version of this figure can be viewed online.)

monolayer CuPc in terms of the aforementioned first layer effect, one expects much larger EF from tBLG with specific θ . Interestingly, the observed mode-dependent enhancement, also observed for Pc on graphene [7], indicates that a vibration symmetry dependence exists for the Raman enhancement for this effect. Symmetry wise, it is known that D_{nh} symmetry of molecule has strong molecule-graphene structural effect [11]. In group theory, CuPc is D_{4h} symmetry which has strong interaction with graphene.

The observed enhancement behavior described above is closely associated with the occurrence of CT between frontier orbitals of CuPc and vHs of tBLG by considering energy diagram of two materials. Fig. 5E is schematic energy diagrams of CuPc and tBLG with $\theta = 12.2^{\circ}$, in which HOMO and LUMO of CuPc are situated at -5.2and -3.5 eV [49], respectively, and E_{vHs} of tBLG ($\theta = 12.2^{\circ}$) is 2.3 eV (see equation (1)) with a Fermi level at -4.57 eV [50]. It has been argued that ground state CT from an underlying graphene to molecule is responsible for GERS [21]. Because ground state CT depends on relative energies of levels between two occupied levels, the DOS of tBLG that are above the HOMO of CuPc would govern the magnitude of the EF of CuPc. However, in the case investigated above, the energy of the lower vHs derived from $10.9^{\circ} < \theta < 13.7^{\circ}$ is below the HOMO of CuPc. Thus, one would expect that a similar DOS exists for tBLG having all of the θ values, and as a result ground state CT would be similar in all cases. However, a singularity exists in the EF for tBLG having $\theta = 12.2^{\circ}$. Therefore, we suggest that the enhancement caused by tBLG is associated with an excited state CT mechanism involving the upper vHs of tBLG and the LUMO of CuPc with a similar energy. If excited state CT from vHs to LUMO is operating in this system, enhanced Raman of CuPc should depend on *E*_{vHs}. Importantly, our results do indicate that when the energy of the upper vHs matches that of the CuPc LUMO, EF is maximized.

electronic structure calculations were performed using DFT (see Experimental for detailed method). Several Moire superlattices (Figs. S5A-E) were generated by constructing unit cells of tBLG using superlattice vector (m, n) and multiplication of unit cells (see superlattice construction in SI). Fig. 6A shows top and side views of the unit cell containing CuPc on tBLG with $\theta = 13.2^{\circ}$ and stacked structure in a slab, respectively. It is noteworthy that precise match of superlattice with $\theta = 12.2^{\circ}$ which displayed the highest EF requires larger (m, n) index and subsequent larger superlattice. Owing to computational cost, we chose 11 and 13.2° tBLGs as model systems to examine the effect when $\theta = 12.2^{\circ}$. For clarity of the notation purposes, in the side view CuPc/tBLG is denoted as CuPc/ SLG₁/SLG₂. Orbital energies of CuPc and DOS of tBLGs with different θ values are given in Fig. 6B. The calculated vHs are consistent with those described in the literature [31,51]. CuPc is stacked with a 27° rotation with respect to the underlying graphene layer (SLG₁), which corresponds to the most stable adsorption configuration [52]. Adsorption energies of CuPC on tBLG (E_{ads}) with varying distance were calculated by using equation (2),

$$E_{\text{ads}} = E_{\text{CuPc/tBLG}} - (E_{\text{CuPc}} + E_{\text{SLG1}} + E_{\text{SLG2}})$$
(2)

where $E_{CuPC/tBLG}$ is the energy of CuPc/tBLG, and E_{CuPc} , E_{SLG1} and E_{SLG2} are respective energies for CuPc, SLG₁, and SLG₂. With the atomic structure fixed, the structure having the most negative adsorption energy was determined fixing the atomic structure and then making the distances separating CuPc from SLG₁ and SLG₁ from SLG₂ at 6, 11, 13.2, 21.8 and 32.2°. This approach gave a minimum energy absorption structure with a CuPc/SLG₁ distance of 3.35 Å and a SLG₁/SLG₂ interlayer distance of 3.45 Å (Table S2).

Fig. 6C presents band structure along high symmetry points and the DOS of CuPc/tBLG with $\theta = 13.2^{\circ}$, along with the partial DOS



Fig. 6. (A) Top and side views of the unit cell for CuPc/tBLG with $\theta = 13.2^{\circ}$. The cell contains 361 atoms with monoclinic unit cell with lattice constant of 21.48 Å. The copper in CuPc was placed on top of a graphene carbon. (B) DOS of bare tBLGs with different θ (colored line) and bare CuPc (black line), respectively. Average frontier orbital energies (HOMO/ LUMO) of CuPc were aligned with the center of the Dirac cone of tBLG. The dashed line indicates a change of VHs according to θ . (C) Band structure and resulting DOS of plyridized CuPc(BLG with $\theta = 13.2^{\circ}$. (black) together with the PODS of CuPc (red) and tBLG (blue). (D) The relationship between mixed state occurrence and the product of the contributed fraction of CuPc (χ_{CuPc}) and SLG₂ (χ_{SLG2}). LUMO orbitals near upper vHs (within vHs \pm 0.25 eV range) were taken into account. The fraction of orbitals that satisfy the condition of 5% or more for both χ_{CuPc} and χ_{SLG2} is 0.13%, 2.05%, 1.36%, 0.22% and 0.00% for 6, 11, 13.2, 21.8 and 32.2°, respectively. (A colour version of this figure can be viewed online.)

(PDOS) of both CuPc and tBLG. Orbitals of CuPc that correspond to the PDOS, seem to have unchanged energies regardless of the kpoint. However, slight band structure shifts occur between the high symmetry points (left panel in Fig. 6C), as a consequence of interactions between nearby tBLG orbitals independent of θ (Figs. S6A–D). To quantify the interactions between the adjacent orbitals, we dissected the orbitals of interest into contributions associated with CuPc, SLG1 and SLG2. Analysis of the occurrence of states near vHs that satisfies the condition where each composition is greater than 5% is given in Fig. 6D (see SI for detailed explanation). The results show that a relatively large amount of mixing occurs in LUMO of CuPc/upper vHs of tBLG with θ values of 11° and 13.2°, confirming that the interaction between CuPc and tBLG near vHs is greater when θ is in the 11–13.2° range. Likewise, such graphs of frontier orbitals of CuPc/vHs of tBLG (Fig. S7A), HOMO of CuPc/lower vHs of tBLG (Fig. S7B) show similar trends. Obviously, the closer vHs of tBLG is to the HOMO/LUMO gap of CuPc, the stronger would be the CT interaction.

The Stokes Raman scattering intensity corresponding to general resonance Raman scattering, can be expressed as shown in equation (3) [21,53,54],

$$I(E_L) = JDOS \times \left| \frac{\langle f | M_{e-r} | b \rangle \langle b | M_{e-ph} | a \rangle \langle a | M_{e-r} | i \rangle}{(E_L - E_g - i\gamma_a) (E_L - E_g - E_{ph} - i\gamma_b)} \right|^2$$
(3)

where $|i\rangle$ is the initial state, $|a\rangle$ and $|b\rangle$ are two intermediate

states, $|f\rangle$ is the final state, H_{e-r} and H_{e-ph} are the matrix element of the respective Hamiltonians of the radiation of the light and the electron-phonon coupling, $E_{\rm L}$ is the energy of the incident light, $E_{\rm g}$ is the energy of the electron transition, $E_{\rm ph}$ is the phonon energy (or vibrational energy), and γ_a and γ_b are the damping constants which are related to the lifetimes of the two intermediate states $|a\rangle$ and $|a\rangle$ b>. Inspection of the denominator of equation (3), which is associated with excitation transition of Raman process, shows that the Raman intensity I depends on the excitation laser energy $E_{\rm L}$, and that the Raman intensity reaches a maximum when $E_{\rm L} = E_{\rm g}$ or $E_L = E_g + E_{ph}$. For the case of CuPc, $E_L = 2.33$ eV, $E_g = 1.41 - 1.7$ eV, and $E_{ph} = 0.17$, 0.18 and 0.19 eV for A_{1g}, E_{2g}, and A_{1g} modes. Therefore, CuPc does not meet the resonance condition with $E_{\rm L}$ (left of Fig. 5E). Excitation is also possible for tBLGs having specific θ values. The E_g of tBLG with $\theta = 12.2^\circ$ is 2.32 eV, which matches E_L precisely (process 1 of Fig. 5E). Excited electrons that meet the resonance condition can be utilized for excited state CT to CuPc (process 2), subsequent relaxation (process 3) in CuPc, and final relaxation (process 4) for momentum conservation, further supporting the proposal that matching vHs with LUMO induces large EF. However, as the results of the DFT calculations show, tBLG with $\theta = 11^{\circ}$ exhibits a much higher state crossover (corresponding to process 2) than tBLG with $\theta = 13.2^{\circ}$ does. Moreover, the denominator in equation (3) for tBLG with $\theta = 13.2^{\circ}$ is much smaller than that for tBLG with $\theta = 11^{\circ}$ which has $E_{\rm vHs} = 2.12$ eV, which means that it has a greater excitation transition. Also, the contribution of $E_{\rm ph}$ (0.198 eV and 0.318 eV for G and 2D bands of SLG) also results in

smaller denominator in equation (3) for tBLG with $\theta = 13.2^{\circ}$. The tradeoff between efficient excited state CT and resonant excitation plays an important role in determining the Raman EF of CuPc. Overall, two criteria which include significant mixed states between CuPc and tBLG and resonant condition of tBLG and excitation laser are necessary to fulfill tBLG-based greater Raman enhancement of CuPc.

One might question the reason for focusing on specific θ range of tBLG. The growth itself produces tBLG with all possible θ . However, the RIS setup which is based on refractive optics in this study limits the observation range to the visible light (*i.e.*, 450–650 nm). Usage of mirror-based reflective optics can extend the detection range of RIS further which has been demonstrated already [15,32]. Moreover, R' band which is another rotation-induced band like R band is active for tBLG with θ below 10° [35], Raman spectroscopy still verifies θ of tBLG. On the other hand, since transmission electron microscopy (TEM) which is an accurate method to determine θ of tBLG unequivocally [36] requires transfer technique of sample to a TEM grid without disturbing θ , and needs post CuPc deposition for every θ of tBLG, the combined optical methods of RIS and Raman spectroscopies might be an alternative way to characterize tBLG and related effect.

3. Conclusions

In the study described above, we showed that when the van Hove singularity of tBLG matches the HOMO/LUMO levels of CuPc, maximal Raman enhancement of CuPc occurs. In the effort described above, hexagonally grown stacked few lavered graphene tBLG was prepared by using the slow chemical vapor deposition method. Initial characterizations of tBLG were conducted by utilizing two widefield optical methods including RIS and Raman spectroscopy. RIS enables accumulation of spatial and spectral information about the tBLG, which can be utilized to determine θ values. Moreover, using widefield Raman spectroscopy, we found that tBLG displays R band, confirming that θ has an average angle difference of 0.26° ranging from -0.02° up to 0.62° . Uniformly deposited CuPc on tBLG, fabricated by using vacuum thermal evaporation, displays θ -dependent Raman enhancement in which tBLG with $\theta = 12.2^{\circ}$ exhibits the greatest EF among various tBLGs. The results of DFT calculations showed that this enhancement is caused by interaction of tBLG with CuPc. The vHs of tBLG with specific θ values and the frontier orbitals of CuPc have similar energies and therefore a large crossover of states exists between these substances. This state mixing facilitates charge transfer from tBLG to CuPc, causing enhanced Raman signals that are greater than those promoted by single layer graphene. Because controlling θ is experimentally achievable via controlled stacking of large-area monocrystalline SLG [16] using the deterministic transfer method [55], few atom thick inert sheets can be fabricated to enhance charge transfer-mediated Raman enhancement. Like SLG [42], this material can be potentially useful to enhance Raman signals of nanostructured Au, Ag and Cu further by covering with tBLG or protect organic compounds from external environment without compensating Raman enhancement, as seen by carbon nanotubeencapsulated organic dye [56].

4. Experimental

4.1. Materials and methods

Copper foil (purity >99.96%, Cat. No.: Cu-113213) was purchased from Nilaco Corp. (Japan). Acetic acid (99.5%) and isopropyl alcohol (99.5%) were obtained from Samchun chemical (Seoul, Republic of Korea). All gases including N₂ (purity over 99.99%), H₂ (purity over 99.9999%) and CH₄ (purity over 99.95%) were purchased from Donga Gas (Seoul, Republic of Korea). PMMA (molecular weight: 950 kDa, 2% dilution in anisole, MicroChem, Kayaku Advanced Materials, Inc., MA USA) was used as a protective layer for transferring graphene to a desired substrate. CuPc was purchased from TCI (β-form, Cat. No.: 147-14-8, Japan). Millipore quality deionized water with a resistivity greater than 18 M Ω was used to wash and transfer graphene samples. Microscopes and objective lenses were purchased from Olympus (Japan). Other optical elements such as convex lenses and bandpass filters were purchased from Thorlabs (NJ, USA). Optical microscope measurements were conducted using an upright microscope (BX51) equipped with $100 \times$ objective lens (numerical aperture (NA) = 0.90) and a CMOS detector (3.6 μ m/ pixel, 1280 \times 1024, DCC1645C, Thorlabs, NJ, USA). Thermal evaporation of CuPc was performed with evaporation rates of 0.1 Å/s at 296 °C under vacuum (*i.e.*, 10^{-7} torr) using a custom-made thermal evaporator. Prior to CuPc deposition, careful calibration of CuPc thickness was conducted by correlating in situ quartz crystal microbalance and ex situ AFM measurements. Height topographies were acquired by tapping mode using a commercially available AFM (NX10, Park systems, Republic of Korea) in which Al-coated silicon cantilever with a spring constant 37 N/m, a resonance frequency of 300 kHz, and quoted radius of *ca*. 6 nm (ACTA, App Nano, CA, USA) was utilized. Typically, a 512 \times 512 pixel image was collected. AFM images were baseline corrected by using polynomial fitting.

4.2. Graphene synthesis and transfer

tBLG grains were synthesized using the reduced pressure CVD method with a tube furnace (max. temp.: 1100 °C, Cat. No.: TF55030C-1, Lindberg Blue/M Mini-Mite, Thermo Fisher Scientific, MA, USA) and a oil-free scroll pump (max. pressure: *ca*. 10^{-3} torr, XDS10, Edwards Vacuum, England), according to previous literature descriptions [26,27]. A strip form of Cu foil (1 cm × 7 cm) was carefully pre-annealed at 1030 °C for 12 h under a flow of a mixture of Ar and H₂ (10 sccm and 100 sccm, respectively) to remove oxygenated copper and reorganize the copper surface [57]. Graphene was grown for 1 h under a flow of 1 sccm CH₄, 60 sccm H₂ and 10 sccm Ar at 950 °C. After stopping the CH₄ flow, the oven was cooled to room temperature at a rate of *ca*. 25 °C/min. Optional visualization of partially grown graphene on Cu substrate was achieved by air oxidation of a portion of the Cu strip at 160 °C [58].

4.3. Graphene transfer process

Using a previously described method [26], PMMA solution was spincoated at 3000 rpm for 60 s onto the graphene-grown Cu foil. The underlying copper foil was removed by submersion in a 0.1 M ammonium persulfate solution for 5 h, and the resulting PMMA film on graphene was initially transferred to a piranha solutioncleaned slide glass and subsequently washed with DI water twice. Finally, PMMA-supported graphene was gently transferred to a Si substrate (285 nm of SiO₂ thickness, Lot#:7400383-603-Z, Shinetsu, Japan) which was later slightly-tilted to facilitate water runoff and drying. The sample was dried in a vacuum oven (*i.e.*, 30 mTorr) at the room temperature. The sacrificial PMMA film was removed by dipping into a hot acetone bath overnight. The substrate was gently washed sequentially with acetone and isopropyl alcohol, and dried using a N₂ stream.

4.4. RIS measurements

The RIS setup was custom-made by using excitation part of fluorescence spectrophotometer (Nanolog 3–21, Horiba, Kyoto,

Japan) consisting of 300 W Xe arc lamp (220–1000 nm, 300 W, UXL-300D-O, Ushio, CA, USA), subtractive double monochromators, and sample chamber according to the literature description [27]. A beam expander combining three convex lenses [LB1811-A (f = 35.0 mm), LB1761-A (f = 25.4 mm) and LB1676-A, f = 100.0 mm] focused monochromatic light onto the back focal plane of a long working-distance 50 \times objective (LMPlanFl, NA = 0.5) installed in an upright microscope (BX41 M). Usage of the long working distance objective minimized chromatic aberration originating from wide excitation range. The image was recorded by using CCD detector (Cool SNAP MYO, pixel size: $4.54 \times 4.54 \ \mu m^2$, 1940×1460 pixels, Teledyne Photometrics, AZ, USA). The image recording speed and the scanning speed of double monochromator generating 1.91-2.81 eV light were synchronized. Reflection images and composite images were processed using the previous reported method [27] using Image[[29].

4.5. WFR measurements

Micro, line and widefield Raman G-band imaging measurements were made by using a custom-made Raman setup with a 532 nm laser (Cobolt, Hübner Photonics, Germany) with either $50 \times \text{ or } 100 \times \text{ objective lenses}$ ((LMPlanFL, NA = 0.5 or MPlan, NA = 0.90, respectively) mounted in an upright microscope (BX50) which was described in our previous reports [26,27]. Micro Raman spectra were acquired for 100 s with a laser power under 1 mW. Line and WFR were acquired for 300 s with a laser power under 200 mW, respectively. For the imaging mode, scattered light was filtered by a bandpass filter (FB580-10, FWHM = 10 nm), and collected for 300 s by a spectral CCD (Syncerity, 1024×256 pixels, pixel size: 26 μ m \times 26 μ m, Horiba, Kyoto, Japan) with open slit (7 mm) and mirror grating mode to obtain G band image. The intensity of all Raman spectra was normalized and calibrated relative to a Si peak of 520.89 cm⁻¹ as the standard. Especially, line spectra of several CCD pixels during WFR have been averaged to produce average value with standard deviation. Typically, the smallest tBLG domain with 12 μ m² provides exceeding *ca*. 15 pixel points to be averaged considering $100 \times$ magnification and pixel size of spectral CCD. 2D band analysis of CuPc with tBLG was provided in SI and Fig. S8.

4.6. DFT calculations

Electronic structures of CuPc, tBLG and CuPc/tBLG were calculated using DFT implemented in the a Vienna Ab Initio Simulation Package (VASP) [59]. The structure of CuPc was optimized in a cube with a side length of 30 Å using Perdew-Burke-Ernzerhof (PBE) functional [60] until the Hellmann-Feynman forces reached less than 0.05 eV/Å. The cut-off energy was 400 eV with accurate precision mode and the convergence criterion for the self-consistent loop was 10^{-6} eV. The resulting CuPc structure is given in Table S3 and is in excellent agreement with the experimental structure [61]. The calculated HOMO/LUMO gap of the CuPc molecule is 1.41 eV, which agrees fairly well with the experimental value of 1.5-1.7 eV [49,62]. For the case of tBLG, superlattice construction was performed according to a unit vector (*m*, *n*) elaborated in SI, and physical parameters are listed in Table S4 according to the literature [63]. With atomic positions fixed, the structure that gives the minimum energy was determined by changing the two distances (CuPc/SLG₁ and SLG₁/SLG₂) for angles between 6, 11, 13.2, 21.8 and 32.2°. The spin polarized calculations were performed, and the Brillouin zone was sampled from the Γ point only. The results are given in Table S2. For the CuPc/tBLG structure optimization and electronic structure calculations, we used local spin density approximation [64] with +U method (LSDA + U) [65] to describe

d orbitals in Cu precisely with 7.1 eV of U-J value [66]. Band structure of the CuPc/tBLG was calculated along the symmetry points in the first Brillouin zone of hexagonal lattice $\Gamma \rightarrow K \rightarrow M \rightarrow \Gamma$ containing 10 points in each path (Fig. S5). The relative occurrence in Fig. 6C were counted for orbitals that exist along the paths and satisfy the condition mentioned in main text. The Brillouin zone for the DOS calculation of bare tBLG was sampled as approximately $400/L \times 400/L \times 1$ where *L* is the lattice constant. For the DOS of CuPc/tBLG with $\theta = 13.2^{\circ}$, $14 \times 14 \times 1$ *k*-points grid was employed and the Gaussian smearing with 0.05 eV was used for all of the DOS calculations.

CRediT authorship contribution statement

Younghoon Cheon: and prepared samples and conducted characterizations. **Youngsam Kim:** and performed theoretical calculations on tBLG. **Minsuk Park:** helped with sample preparations. **Jehyun Oh:** analyzed EF of tBLG. **Eunhye Koo:** prepared samples and conducted characterizations. **Eunji Sim:** performed theoretical calculations on tBLG. **Sang-Yong Ju:** conceived the idea and wrote the manuscript, Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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Y. Cheon, Y. Kim, M. Park et al.

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Excited State Charge Transfer Promoted Raman Enhancement of Copper Phthalocyanine by Twisted Bilayer Graphenes

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^{*} To whom correspondence should be addressed. Tel: +82-2-2123-5633. E-mail: esim@yonsei.ac.kr (Eunji Sim); Tel: +82-2-2123-5639. E-mail: syju@yonsei.ac.kr (Sang-Yong Ju) Figure S7. The relationship between mixed state occurrence and the product of the contributed

Superlattice construction & orbital interaction analysis: Initially, several superlattices were constructed by placing graphene in unit cells. (m, n) vector in which m and n are both integers is defined by hexagonal unit cell with four vertices with carbons overlapped on top of each other.[1] Moire superlattice of a tBLG at rotation angle θ between the two monolayers can be described by lattice vectors,

$$v_1 = ma_1 + na_2, v_2 = na_1 + (m+n)a_2$$

 $v_1' = na_1 + ma_2, v_2' = -ma_1 + (m+n)a_2$

where, a_1 and a_2 are the primitive lattice vectors of A-A stacking bilayer graphene, v_1 and v_2 are lattice vectors of the first layer of graphene, while v'_1 and v'_2 are lattice vectors of another layer. Unit cell dimension *L* and chiral angle θ were determined by using the following equations:

$$L = a\sqrt{m^{2} + mn + n^{2}}$$
$$\theta = \frac{1(m^{2} + 4mn + n^{2})}{2(m^{2} + mn + n^{2})}$$

where *a* is lattice parameter (*i.e.*, 2.464 Å) based on 1.42 Å of C–C distance of graphene. In this manner, (3,4), (2,3), (1,2), and (1,3), unit cells were constructed. To construct CuPc/tBLG cell, the unit cell of tBLG was repeated as described in Table S2. The distances between the CuPc molecules in the CuPc/tBLG repeated cell were 8.38, 10.52, 6.27, 4.36, and 11.45 Å for 6, 11, 13.2, 21.8, and 32.2° tBLG, respectively. It is noteworthy that precise match of superlattice with $\theta = 12.2°$ which displayed the highest EF requires larger supercell with larger (*m*, *n*) index, as indicated by unitcell size in Supporting Figures. Owing to computational cost, we opt to choose 11 and 13.2° tBLGs as model systems to examine the effect when $\theta = 12.2°$.

In order to investigate the interaction between moieties, the orbital of CuPc/tBLG was decomposed as follows:

$$\Psi_{\text{CuPc/tBLG}} = \sqrt{\chi_{\text{CuPc}}} \psi_{\text{CuPc}} + \sqrt{\chi_{\text{SLG1}}} \psi_{\text{SLG1}} + \sqrt{\chi_{\text{SLG2}}} \psi_{\text{SLG2}}$$

where ψ is a moiety projected wavefunction and χ represents the orbital contribution of the

corresponding moiety. While CuPc and SLG₁ are stacked in all systems regardless of the twist angle of tBLG, SLG₂ has no direct contact with CuPc (distance~6.8Å). In other words, large partial contribution of CuPc (χ_{CuPc}) and SLG₂ (χ_{SLG2}) at the same time represents large interaction between CuPc and tBLG. As $\chi_{CuPc} \times \chi_{SLG2}$ an indicator, the occurrence histogram of the number of states with respect to $\chi_{CuPc} \times \chi_{SLG2}$ values was investigated to analyze the interaction strength between tBLG and CuPc (see Figrues 6D and S7). In this case, for clarity, the states with χ_{CuPc} or $\chi_{SLG2} < 0.05$ (i.e., less than 5% contribution) were ignored.

2D band shape of tBLG with CuPc according to θ : 2D band shape in Raman spectrum was investigated as shown in Figure S8. Raman spectra show that 2D band obtained from 12.6° exhibits most intense signal, showing 2-3 times greater than those of other tBLGs. Although this is in line with the aforementioned G band enhancement with tBLG with same angle, the intensity is much smaller. Those observations are in agreement with the literature.[2] In addition, band shape was best-fitted with Lorentzian shape, rather than four components observed in bBLG[3] and show 36-44 cm⁻¹ range of full width at half maximum (FWHM) with tBLG with 12.6° as smallest.

Detailed Raman analysis of CuPc/SLG: Raman spectra of SLG (Figure S4A) and CuPc/SLG (Figure S4B) were displayed from several spots. Comparison of those points were obtained by mapping in doping and strain coordinates which was adapted from the literature.[4] Lee and coworker[4] determined that Raman G and 2D bands of SLG are utilized to determine strain and doping contributions in which, as temperature increases, SLG supported on SiO₂/Si substrate undergoes upshifts of G and 2D band positions owing to substrate-induced *p*-doping and surface-topography induced tensile strain. In our experiment, the used laser line is 532 nm and the charge neutral Raman signature is interpolated.[5] Briefly, ω_G and ω_{2D} of charge-neutral suspended graphene (1581 and 2667.5 cm⁻¹, respectively)[6] are added after correction of energy dispersive ω_{2D} by excitation shift factor (i.e., 88 cm⁻¹/eV).[7] Using this as a reference point, two $\Delta\omega_{2D}/\Delta\omega_G = 0.7$)[4, 8-10] along with scales are drawn to distinguish main contribution of SLG, as shown in Figure S4C. In Figure S4C, Raman data, mean values with distributions from SLG and SLG/CuPc were displayed along with

SLG which are determined from the similar SLG sample.[5] Clearly, initial SLG sample has similar average (ω_G , ω_{2D}) = (1593, 2679) as compared to those (1591, 2679) of SLG.[5] However, CuPc/SLG sample displayed average (ω_G , ω_{2D}) = (1588, 2694) in which ω_G (ω_{2D}) are downshifted (upshifted) as compared to those of the initial SLG. This result suggests that slight *n*-doping and tensile strain occurs after CuPc deposition. Clearly, *n*-doping of SLG in CuPc/SLG occurs owing to CT. The possible origin of tensile strain from CuPc/SLG sample is an extended configuration of SLG due to π - π interaction with CuPc and simultaneous decoupled interaction with substrate.

Figure S1. Schematics of beam expander in which second convex lens has a focal length of 500 mm to reach the backfocal plane of objective lens so that the objective lens has a widefield illumination.



Figure S2. Determination of layer thickness by optical and AFM measurements. (A) OM image of segmented graphene regions and (B) corresponding RIS image. (C) Corresponding AFM height topography and (D) height profile of dotted line in (C).



Figure S3. θ_R determination based on experimental R band plot from ref. [11]. Inset: two phonon process of R band. E_L and E_S are laser energy, and scattered energy, respectively. Q_{inter} denotes intervalley phonon scattering. *K* and *K*' denote high symmetry points in the Brillouin zone.



Figure S4. G and 2D band shift of SLG before and after CuPc deposition. Raman spectra of SLG (A) before, and (B) after CuPc deposition. Green lines are Lorentzian fitting of graphene vibrational bands. (C) Decomposition of G and 2D band positions into strain and doping contributions. Charge neutral point = (1581, 2261) was obtained from suspended SLG. Blue square denotes G and 2D band positions obtained from SLG on a SiO₂ substrate from ref.[5]. e_n and e_T denote doping and strain contributions in which + and - signs of e_T stands for respective tensile and compressive strains, + and - signs of e_n denote p- and n-doping, respectively. Each quadrant was denoted by Q. Inner axis denotes band shift ratio ($\Delta \omega_{2D} / \Delta \omega_G$) according to doping and strain, respectively.



Figure S5. Unit cells of tBLGs with θ = (A) 9.4, (B) 11, (C) 13.2, (D) 21.8, and (E) 32.2°. Note that unit cells with simple unit vectors have been selected to minimize calculation cost.



Figure S6. (A-D) Band structure of CuPc/tBLG with $\theta = 6$, 11, 21.8, and 32.2°. The Dirac cone is formed at the K point for CuPc/tBLG with $\theta = 6$, 11, and 13.2° (Figure 6C). However, band structures of 21.8 and 32.2° CuPc/tBLG have closed band gap at the Γ point due to the Brillouin zone sampling of the superlattice. (E) The Γ point of the CuPc/tBLG superlattice overlaps the K point in the Brillouin zone (BZ) of the tBLG unit cell.



Figure S7. The relationship between mixed state occurrence and the product of the contributed fraction of CuPc (χ_{CuPc}) and SLG₂ (χ_{SLG2}) considering (A) HOMO/LUMO orbitals and upper/lower vHs, and (B) HOMO and lower vHs only.



Figure S8. 2D band of CuPc/tBLG according to θ . For comparison, that of SLG was presented.

Number in bracket indicates FWHM.



OM image	G band image	RIS image	Domain size [µm ²]	R band position [cm ⁻¹]	R band FWHM $[cm^{-1}]$	θ _R [°]	$E_{\rm vHs}$ [eV]	vHs FWHM [eV]	$ heta_{ m vHs}$ [°]	Avg θ [°]	$ heta_{ m R}$ - $ heta_{ m vHs}$ [°]
		-	20.3	1480.1	20.0	14.04	2.52	0.28	13.42	13.73	0.62
	1		134	1491.6	11.0	12.77	2.39	0.24	12.60	12.69	0.17
<u></u>	1	1	26.4	1489.5	8.0	12.81	2.37	0.28	12.47	12.64	0.34
			60.3	1493.4	11.9	12.55	2.37	0.25	12.47	12.51	0.08
	5	X	52.9	1494.1	16.1	12.49	2.37	0.25	12.47	12.48	0.02
		4	30.3	1494.7	15.0	12.41	2.29	0.22	11.99	12.20	0.42
1225	-	-	12.3	1494.5	16.0	12.45	2.29	0.20	11.99	12.22	0.46
		1	27.4	1499.3	11.2	11.93	2.26	0.21	11.80	11.87	0.13
		5/	196	1499.2	22.4	11.97	2.22	0.29	11.57	11.77	0.40
			148	1503.7	8.3	11.44	2.18	0.28	11.33	11.39	0.11
$\overline{\mathbb{D}^2}$			33.7	1505.8	15.2	11.25	2.27	0.29	11.27	11.26	-0.02
		0	55.5	1505.4	10.3	11.28	2.15	0.21	11.15	11.22	0.13
Ś			25.7	1504.3	11.9	11.37	2.12	0.20	10.98	11.18	0.39
****	ø		20.7	1507.7	9.8	11.08	2.11	0.30	10.92	11.00	0.08
The second	Pa		22.2	1507.0	11.6	11.15	2.07	0.27	10.69	10.92	0.46
Average difference								0.26			

Table S1. Measurements of various tBLGs and corresponding θ_{R} , θ_{vHs} , and θ (scale bar: 5 µm).

Table S2. Relative adsorption energy (eV) of CuPc/SLG₁/SLG₂ based on equation **2**. The distances displaying energy minimum are in boldface. For the CuPc/tBLG with θ = 32.2°, the additional calculation of the Brillouin zone sampling 2 × 2 × 1 was performed and is denoted with [†]. We choose the most stable distance combination that showed up mainly: 3.35Å (CuPc/SLG₁) and 3.45Å (SLG₁/SLG₂).

tPI G with A	- 6°	CuPc/SLG1 distance (Å)			
(BLO with 0 = 0)		3.25	3.35	3.45	
	3.35	0.153	0.150	0.208	
SLG ₁ /SLG ₂ distance (Å)	3.45	0.003 (0.001 [†])	0.000 (0.000 [†])	0.058	
	3.55	0.076	0.074	0.132	

tBLG with $\theta = 11^{\circ}$		CuPc/SLG ₁ distance (Å)			
		3.25	3.35	3.45	
	3.35	0.060	0.058	0.117	
SLG ₁ /SLG ₂ distance (Å)	3.45	0.001 (0.375 [†])	0.000 (0.000 [†])	0.059	
	3.55	0.179	0.179	0.238	

tBI G with A-	13 2º	CuPc/SLG ₁ distance (Å)			
(BLO WITH 0 - 15.2)		3.25	3.35	3.45	
	3.35	0.023	0.021	0.080	
SLG ₁ /SLG ₂ distance (Å)	3.45	$0.001 \\ (0.002^{\dagger})$	0.000 (0.000 [†])	0.059	
	3.55	0.140	0.139	0.199	

tPI C with A-	21.8°	CuPc/SLG1 distance (Å)			
1DLO WITH U = 21.8		3.25	3.35	3.45	
	3.35	0.698	0.034	0.146	
SLG ₁ /SLG ₂ distance (Å)	3.45	0.000 (0.000 [†])	$0.005 \ (0.078^{\dagger})$	0.171	
	3.55	0.107	0.111	0.181	

tBI G with A-	32.20	CuPc/SLG ₁ distance (Å)			
(BLO with 0 - 52.2)		3.25	3.35	3.45	
	3.35	0.708	0.031	0.140	
SLG ₁ /SLG ₂ distance (Å)	3.45	0.000 (0.012 [†])	0.001 (0.000 [†])	0.733	
	3.55	0.907	0.902	0.304	

Properties		Experimental[12]	PBE	Abs. difference
Bond length (Å)	Cu-N1	1.935	1.963	0.028
\rightarrow	N1-C2	1.366	1.379	0.013
C8	C2-N2	1.328	1.327	0.001
	C2-C3	1.453	1.457	0.004
	C3-C4	1.4	1.410	0.01
	C3-C5	1.388	1.397	0.009
	C5-C6	1.377	1.395	0.018
\succ	C6-C7	1.4	1.408	0.008
Angle (°)	C2-N1-C1	107.3	108.5	1.2
	N1-C2-N2	127.6	127.8	0.2
	N1-C2-C3	110.4	109.2	1.2
	C2-N2-C8	122.2	123.0	0.8
	C2-C3-C4	106	106.5	0.5
	C4-C3-C5	121.1	121.2	0.1
	C3-C5-C6	118.0	117.6	0.4
	C5-C6-C7	121.0	121.3	0.3

Table S3. The optimized structure parameters of CuPc via PBE functional, and comparison

experimental data.[12]

Table S4.Information of the Moire superlattices. θ , N, and L are the twisted angle, the number of
atoms in the unit cell and lattice constant of Moire superlattice correspondingly. k-point
sampling in reciprocal space from the literature[1] is used for unit cell calculations. The
last column is the lattice constants ratio between CuPc/tBLG unit cells and tBLG unit
cells.

(<i>m</i> , <i>n</i>)	$ heta\left(^{\circ} ight)$	Ν	L (Å)	<i>k</i> -point sampling[1]	CuPc/tBLG Unit cell
(1, 3)	32.2	52	8.8697	$5 \times 5 \times 1$	$3 \times 3 \times 1$
(1, 2)	21.8	28	6.5190	$6 \times 6 \times 1$	$3 \times 3 \times 1$
(2, 3)	13.2	76	10.7403	$4 \times 4 \times 1$	$2 \times 2 \times 1$
(5, 7)	11	436	25.7249	$2 \times 2 \times 1$	$1 \times 1 \times 1$
(5, 6)	6	364	23.5051	$2 \times 2 \times 1$	$1 \times 1 \times 1$

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