Supporting information

Electrochemical Formation of Covalent-Ionic Stage-1 Graphite Intercalation Compound with Trifluoroacetic Acid

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1. Construction of the working electrode

Figure S1 shows the construction of the working electrode. Polytetrafluoroethylene (PTFE) parts are chemically and electrochemically inert to the electrolyte. Platinum mesh provides good electrical contact with the graphite flakes and the electrolyte has free access to the graphite surface.

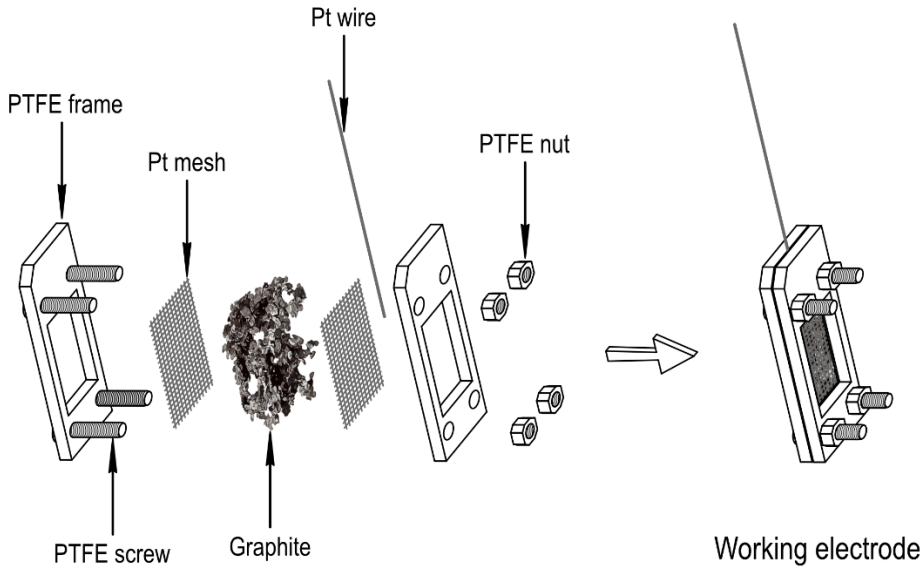

Figure S1. Construction of the working electrode.

2. Stability of the stage-1 CF_3COOH-GIC

The prepared GIC550 product was placed in a glass vial and left open in a fume hood. The sample was then weighed every few days. Figure S2 shows the percent weight loss of the sample over time. XRD patterns of the GIC550, GIC550 after 30 days and also after 90 days are shown in Figure S3.

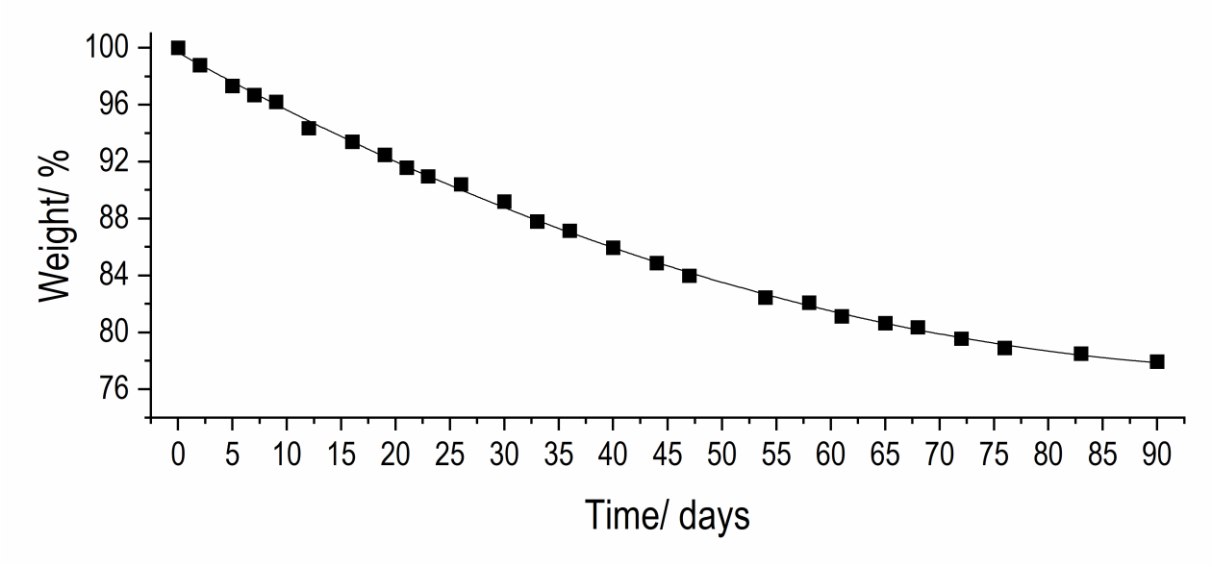

Figure S2. The GIC550 percent weight loss as a function of time.

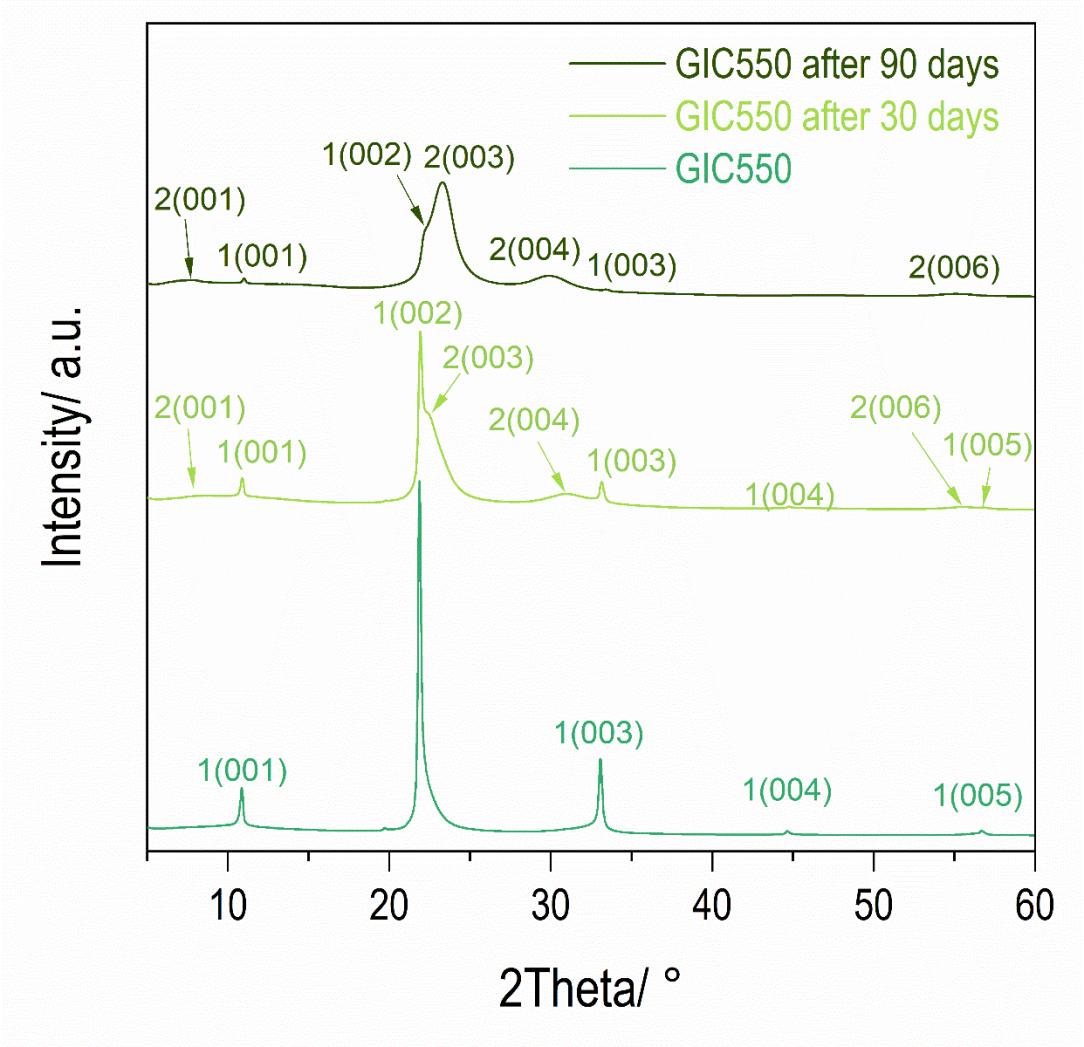

Figure S3. XRD patterns of the GIC550 immediately after the synthesis and after 30 and 90 days.

3. Detailed XRD calculations

Calculated theoretical peak positions for different stages of CF_3COOH-GIC are given in Table S1. Calculated d-spacing for GIC products based on the recorded XRD patterns (Figure S5) are given in Table S2.

Table S1. Calculated theoretical peak positions for CF_3COOH-GIC.

	Peak position/ °			
(00l) index	stage-1 (8.10 Å)	stage-2 (11.45 Å)	stage-3 (14.80 Å)	stage-4 (18.15 Å)
(001)	10.914	7.715	5.967	4.865
(002)	21.928	15.465	11.95	9.738
(003)	33.153	23.287	17.966	14.629
(004)	44.716	31.221	24.033	19.548
(005)	56.783	39.312	30.168	24.503
(006)		47.613	36.393	29.505
(007)		56.189	42.733	34.565
(008)			49.212	39.696
(009)			55.864	44.911
(0010)				50.226
(0011)				55.66

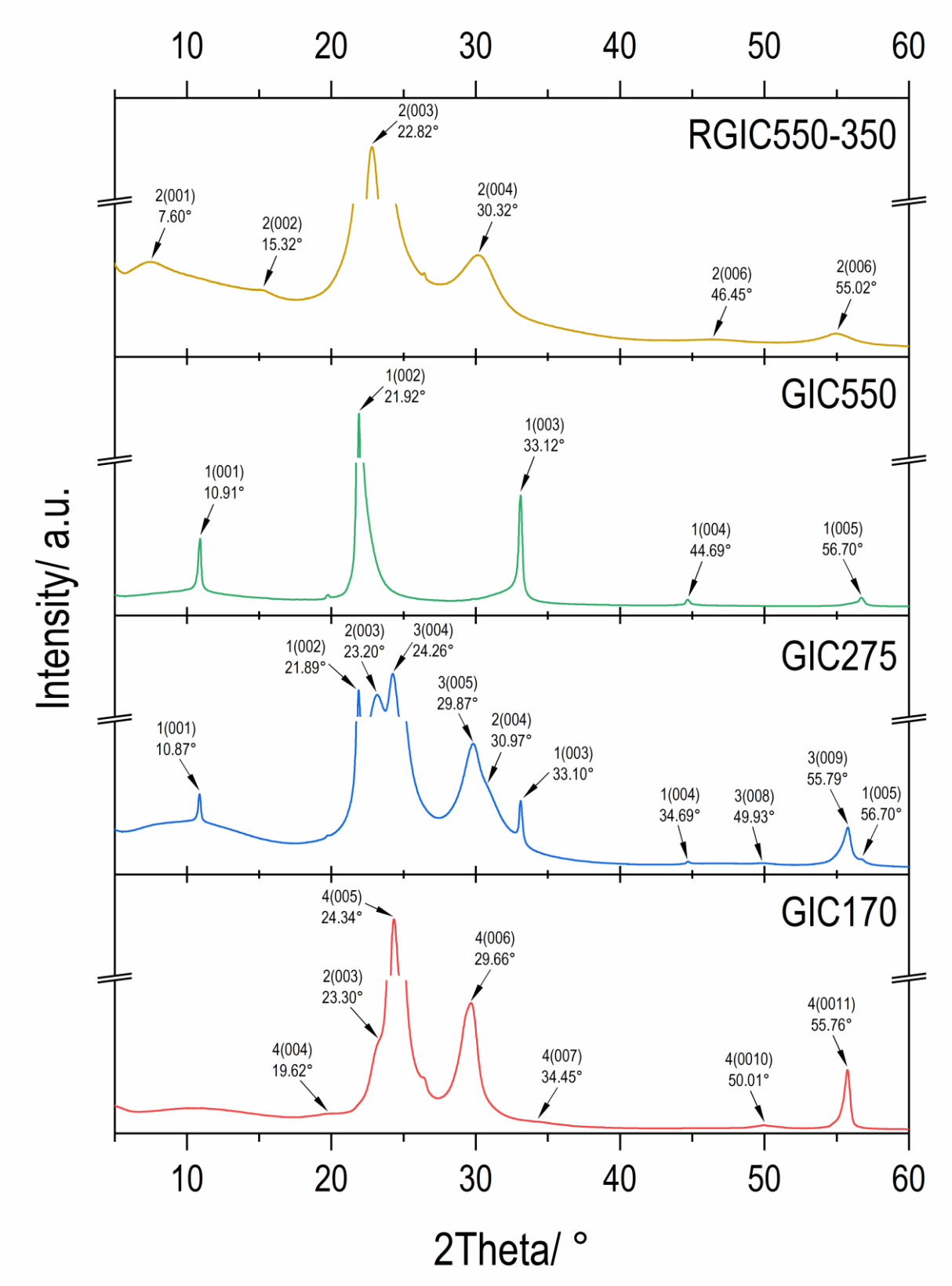

Figure S4. XRD patterns of prepared CF_3COOH intercalated samples detailing all the diffraction peaks.

Table S2. Calculated interlayer spacings d_i for the GIC products based on the recorded XRD patterns.

(00l) index	GIC170				GIC275						GIC550		RGIC550-350	
	stage-2		stage-4		stage-1		stage-2		stage-3		stage-1		stage-2	
	peak position/ °	d_i/ Å	peak position/ °	d_i/ Å	peak position/ °	d_i/ Å	peak position/ °	d_i/ Å	peak position/ °	d_i/ Å	peak position/ °	d_i/ Å	peak position/ °	d_i/ Å
(001)					10.87	8.13					10.91	8.10	7.60	11.62
(002)					21.89	8.11					21.92	8.10	15.32	11.56
(003)	23.30	11.44			33.10	8.11	23.20	11.49			33.12	8.11	22.82	11.68
(004)			19.62	18.08	44.69	8.10	30.97	11.54	24.26	14.66	44.69	8.10	30.32	11.78
(005)			24.34	18.27	56.70	8.11			29.87	14.94	56.70	8.11		
(006)			29.66	18.06									46.45	11.72
(007)			34.45	18.21									55.02	11.67
(008)									49.93	14.60				
(009)									55.79	14.81				
(0010)			50.01	18.22										
(0011)			55.76	18.12										

4. CF_3COOH-GIC formula calculations

We note that the average percent mass increase for the stage-1 GIC is 81%. Based on this knowledge and the Reaction S1, we are able to calculate how many moles of carbon react with 1 mole of trifluoroacetic acid (Equation S2):

$$x_1\mathrm{C} + \mathrm{CF_3COOH} \rightarrow \mathrm{C}_{x_1}\mathrm{CF_3COOH} \quad \text{(S1)}$$

$$x_1 = \frac{m_{\mathrm{graphite}} \cdot M_{\mathrm{CF_3COOH}}}{M_{\mathrm{C}} \cdot (m_{\mathrm{graphite}} - m_{\mathrm{GIC}})} \quad \text{(S2)}$$

where m_{graphite} is the mass of the starting graphite, m_{GIC} is the mass of the stage-1 GIC product, and M_{CF3COOH} and M_{C} are the molar masses of trifluoroacetic acid and graphite, respectively. The calculated x_1 is 11.73. Therefore, it is concluded that one molecule of trifluoroacetic acid "reacts" with 12 atoms of carbon.

The electrical charge passed in the intercalation reaction relates directly to the electron transfer. Based on the charge consumed for the stage-*n* GIC formation, we can calculate the number of carbon atoms positively charged during the formation of stage-1 CF_3COOH-GIC (Equation S3):

$$x_2 = \frac{F}{Q_{\mathrm{GIC}}} \quad \text{(S3)}$$

where F is a Faraday's constant, equal to 96485.33 C mol^{-1}, and Q_{GIC} is a charge consumed for the stage-1 GIC formation in C mol^{-1}. Because electrolyte is also decomposing during the electrochemical formation of stage-1 GIC, we are not able to calculate Q_{GIC} based on a galvanostatic curve. To get the information about the charge consumed for GIC formation we electrooxidize the graphite using linear sweep voltammetry. In this case, we are able to separate the charge used for GIC formation from the charge "lost" for the parasitic reactions (Figure S5). The pure stage-1 CF_3COOH-GIC was formed when the potential 1.66 V was reached. The recorded charge for the GIC formation is equal to 336 C g^{-1} and that is 4032 C mol^{-1} of graphite. Therefore, x_2 calculated using Equation (3) is 23.93. That means that 24 atoms of carbon were "positively charged" during the stage-1 GIC formation. Taking into account the x_1 and x_2 values, 2 trifluoroacetic species react with 24 atoms of carbon, and one of them is negatively charged to counterbalance the positive charge of the carbon atoms, thus the formula of the prepared stage-1 GIC is $C_{24}OOCF_3^+CF_3COO^-$.

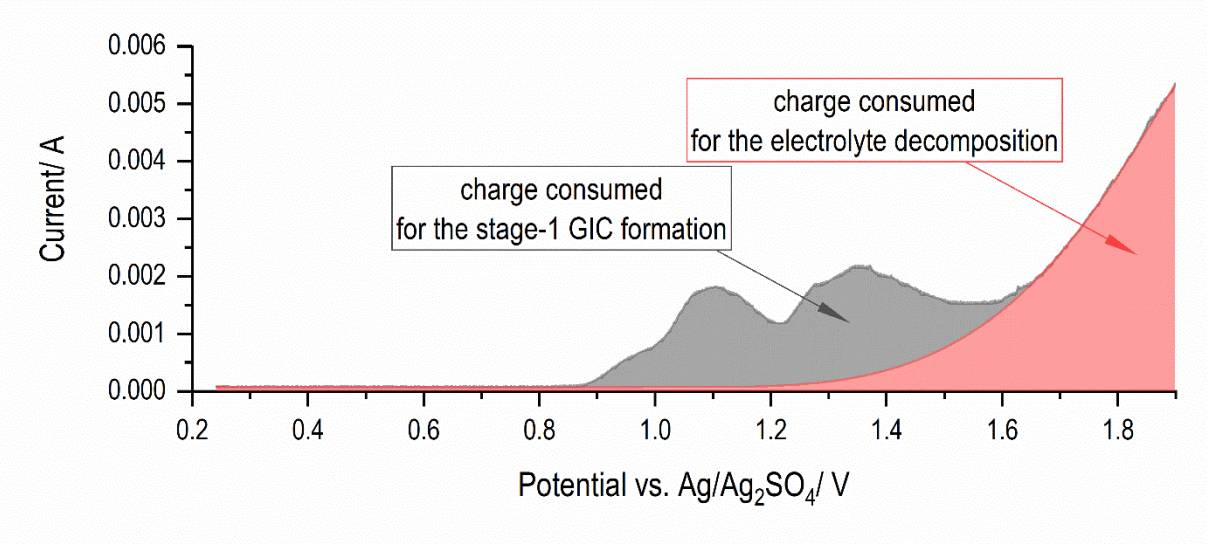

Figure S5. Linear sweep voltammetry curve recorded during the oxidation of graphite in a 0.5 M solution of CH3COONH$_4$ in a 9:1 volume ratio mixture of CF_3COOH and CH_3COOH. Scan rate: 0.025 mV s^{-1}.

5. CF_3COOH-GIC computational details

We performed density functional theory (DFT) calculations to understand structures of GICs with trifluoro acetic acids for the stage-1 and stage-2 intercalation stage. We conducted two different calculations to investigate energetics of possible molecular configurations. First, we conducted periodic boundary calculations to evaluate 2D graphene layers and intercalated CF_3COO^-, $CF_3COO\cdot$ or CF_3COOH. In addition, we further calculated molecular geometries with cluster systems with a coronene ($C_{24}H_{12}$) instead of the graphene layer since the periodic boundary calculations may not be suitable for the system with two layers with different lattice constants. We did frequency calculations to generate infrared vibrational spectra from the cluster calculation. A goal of the theoretical calculations is to estimate molecular structures of Stage-1 and Stage-2 to compare with experimental results.

The initial structures and atomic charge analysis are described in Figure S6 and Figure S7, respectively. All normal modes from frequency calculations in Molden format is provided as a separate file. Here, the [coronene-$OC(=O)CF_3]^+CF_3COO^-$ shows one imaginary frequency which describes out-of-plane vibrations at the edge. We expect that the hydrogen out-of-plane vibration diminishes as the coronene is replaced by the graphene sheet.

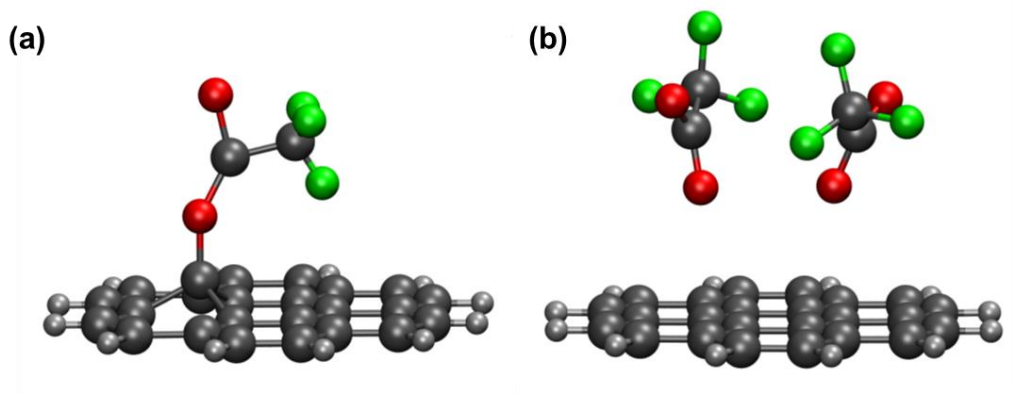

Figure S6 Initial configurations to obtain the structures in Figure 12 in the main text. (a) Coronene-CF_3COO and (b) coronene-$(CF_3COO)_2$ complexes. Depending on the charge of the system, we obtain different bonding characters as described in Figure 12.

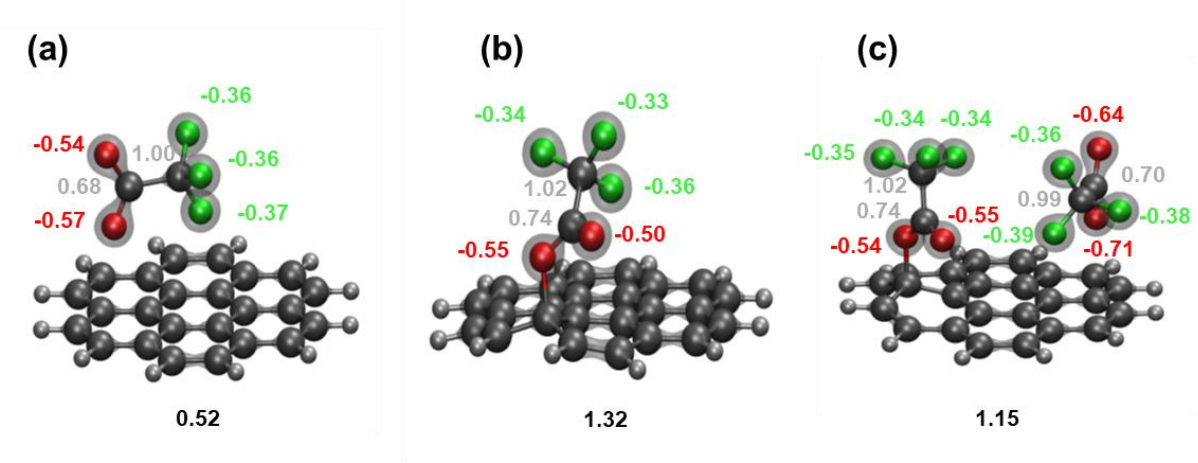

Figure S7. Charge density plots and corresponding atomic charges in coronene complexes. The indicated values represent the natural bond orbital (NBO) atomic charges for carbon (grey), fluorine (green), and oxygen (red) atoms.

We use the Vienna Ab initio Software Package (VASP)[1] with Perdew-Becke-Enzerhof (PBE) functional[2] for periodic calculations. We choose a kinetic energy cutoff as 500 eV, k-points as (4x3x3) and (4x3x2) Monkhorst-Pack grids for stage-1 and stage-2, respectively, and the threshold for the geometry optimization as 0.01 eV/A. In addition, we use Grimme-D3 dispersion corrections to account for van der Waals interactions.[3] To describe a charged unit cell, we consider a uniform counter charge over the unit cell. For coronene complexes, we calculated structures and vibrational frequencies based on density functional theory calculations at the B3LYP/6-31+G* level of theory with the TeraChem (v1.95P) program package.[4] Here, we also use Grimme-D3 dispersion corrections. For the frequency calculations, we use the scaling factor of 0.96.

We performed phonon calculations with the energy cutoff of 700 eV at the optimized unit cell and structure without the dispersion interaction to see the dynamic stability of the structure (d) in Figure 15. The optimized structure shows the covalent bonds between the graphene sheet and CF_3COOs. Figure S8 shows the phonon band which shows mostly positive phonon frequencies except three imaginary frequencies. The three imaginary frequencies correspond to the translational modes at the G-point which should be identically zero analytically. Figure S9 represents three translational modes corresponding to the small imaginary frequencies. We obtain imaginary frequencies due to the numerical instability. We expect the positive-definite phonon frequencies as we increase the numerical accuracy.

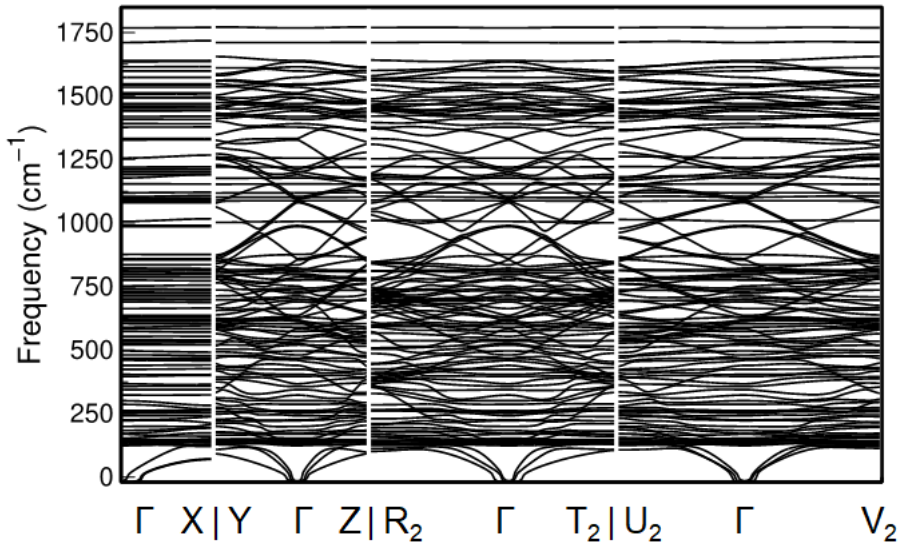

Figure S8. The phonon dispersion relation of the structure (d) of Figure 15 in the main text.

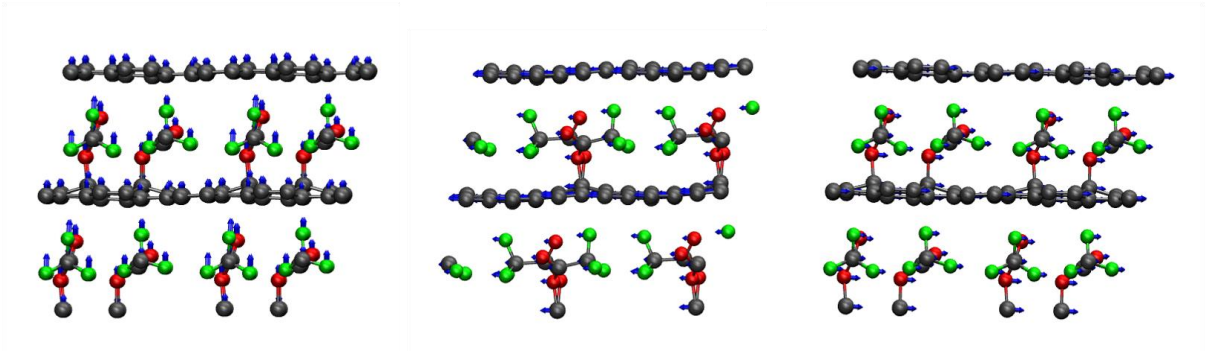

Figure S9. Three acoustic modes with the imaginary frequencies at the G-point.

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(2) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(3) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(4) Seritan, S.; Bannwarth, C.; Fales, B. S.; Hohenstein, E. G.; Kokkila-Schumacher, S. I. L.; Luehr, N.; SnyderJr., J. W.; Song, C.; Titov, A. V.; Ufimtsev, I. S.; Martínez, T. J. TeraChem: Accelerating Electronic Structure and Ab Initio Molecular Dynamics with Graphical Processing Units. *J. Chem. Phys.* **2020**, *152*, 224110.