Supporting Information

Ultrathin Covalent Organic Framework Anchored on Graphene for Enhanced Organic Pollutant Removal

C. Li, P. Guggenberger, S. W. Han, W.-L. Ding, F. Kleitz*
Supporting Information

Ultrathin Covalent Organic Framework Anchored on Graphene for Enhanced Organic Pollutant Removal

Changxia Li,[a] Patrick Guggenberger,[a] Seung Won Han,[b] Wei-Lu Ding,[c] and Freddy Kleitz*[a]

[a] Dr. C. Li, P. Guggenberger, Prof. Dr. F. Kleitz
Department of Inorganic Chemistry – Functional Materials, Faculty of Chemistry, University of Vienna, Währinger Straße 42, 1090 Vienna, Austria
*Correspondence: freddy.kleitz@univie.ac.at
[b] Dr. S. W. Han
Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Daejeon, 34141, South Korea
[c] Dr. W. L. Ding
Beijing Key Laboratory of Ionic Liquids Clean Process, CAS Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
1. Experimental methods

1.1. Materials

All chemicals were purchased from commercial sources and used without further treatment. *p*-Toluene sulfonic acid monohydrate (PTSA, Sigma-Aldrich, ≥ 98.5%), 2,5-Diaminobenzenesulfonic acid (DB-SO₃H, Sigma-Aldrich, ≥ 97.0%), NaOH (Sigma-Aldrich, ≥ 98%), Methylene Blue (MB, Sigma-Aldrich, ≥ 95%), Crystal Violet (CV, Alfa Aesar, ≥ 90%), Rhodamine B (RhB, Fluka), Dimethylacetamide (DMA, Sigma-Aldrich, 99.8%), Ethanol (Alfa Aesar, 94-96%), Acetone (Alfa Aesar, 99.5%), Nitric acid (Alfa Aesar), Congo Red (CR, Alfa Aesar), Methyl Orange (MO, Alfa Aesar), *p*-Phenylenediamine (Pa, Sigma-Aldrich), Benzidine (BD, Sigma-Aldrich).

1.2. Characterization

Wide-angle powder X-ray diffraction (XRD) patterns were carried out on a PANalytical EMPYREAN powder diffractometer equipped with the PIXcel detector (Malvern PANalytical, United Kingdom) in reflection geometry (Bragg–Brentano HD) using Cu Kα₁+₂ radiation, operated at a voltage of 45 kV and a tube current of 40 mA, with a fixed divergence slit of 0.05 mm. Measurements were performed in continuous mode with a step size 20 of 0.013° and a data time per step of 300 s. Nitrogen sorption measurements were measured at −196 °C on a Anton Paar Quantatech Inc. iQ2 instrument (Boynton Beach, FL, USA). All samples were degassed under vacuum at 120 °C for 16 h before measurement. The specific surface area (S_{BET}) was calculated by using Brunauer-Emmett-Teller (BET) calculations from the adsorption data. The pore size distribution plot was obtained from the adsorption branch of isotherms by the quenched solid density functional theory (QSDFT) model (slit/cylindrical pores, N₂ at 77 K on carbon). X-ray Photoelectron Spectroscopy (XPS) spectra were performed on a Thermo Scientific K-Alpha+ X-ray Photoelectron Spectrometer with Al Kα radiation. The samples were pasted and pressed onto the sample holder using carbon tapes for measurement. Scanning electron microscopy (SEM) analyses were performed on an electron microscope Zeiss Supra 55 VP equipped with EDS detector. The accelerating voltages are 5 kV and 20 kV for images and EDS mappings, respectively. Transmission electron microscopy (TEM)
images were obtained using a FEI Titan G2 ETEM at an accelerating voltage of 300 kV. The sample for TEM imaging was prepared by dropping a small amount of ethanol containing a suspended powder sample on a holey carbon film-coated 300 mesh copper grid. Scanning TEM (STEM) mapping was performed using an EDAX Octane Elite T Plus EDS system. Elemental analysis on C, H, N, and S was done using a Eurovector EA3000 CHNS-O analyzer. Zeta potential measurements were performed using a Malvern Zetasizer Nano ZS. The samples were dispersed in water and sonicated for 1 h prior to the analysis. Fourier transform infrared (FT-IR) spectra were measured on a Bruker VERTEX 70v FT-IR Spectrometer with Golden Gate ATR module from Specac. UV-visible adsorption spectra were collected on an Onda Spectrophotometer at room temperature. All samples were analyzed in 1 cm quartz cuvettes. Atomic force microscopy (AFM) images were acquired using a Bruker Multimode 8 instrument. The sample for AFM imaging was prepared by dropping a small amount of IPA/H₂O solution containing sample that has been sonicated for 1 h and spin-coated at 30000 rpm on a Si wafer. Thermogravimetric analysis (TGA) was performed on a Netzsch instrument (STA 449-F3 Jupiter) from 25 to 800 °C at a heating rate of 10 °C min⁻¹ under a N₂ atmosphere.

1.3. Synthesis Procedures
All the syntheses were conducted under air.

**Synthesis of RGO aerogel.** Graphene oxide (GO) was prepared from graphite powder using a modified Hummers’ method, as reported earlier.¹ The 3D RGO aerogel was prepared by hydrothermal reduction of GO aqueous dispersion. Briefly, 18.5 mL of 4.0 mg mL⁻¹ GO solution and 6.2 mL water were stirred for 30 min. Then, the GO aqueous dispersion (3.0 mg mL⁻¹) was sealed in a 50 mL Teflon-lined autoclave. After heating at 120 °C in an oven for 24 h, the autoclave was cooled down to room temperature and 3D RGO aerogel was obtained after freeze-drying.

**Synthesis of COF-SO₃Na.** 1,3,5-triformylphloroglucinol (Tp) was synthesized following the previous literature approach.² 84.7 mg DB-SO₃H (0.45 mmol), 18.0 mg NaOH (0.45 mmol), 6.2 mL of water and 475 mg PTSA (2.5 mmol) were mixed and shaken in a vortex shaker for 2 min. Then, 63.0 mg of Tp (0.3 mmol) was added into the
purple solution and shaken for another 20 min. The orange solution was transferred into an autoclave and heated at 120 °C for 24 h. Then, the product was washed using water (2 × 30 mL) and subsequently by acetone using Soxhlet extraction, then dried overnight under vacuum at 80 °C.

**Synthesis of CGA.** 63.6 mg DB-SO$_3$H, 13.5 mg NaOH, 6.2 mL of water and 357 mg PTSA were mixed and shaken in a vortex shaker for 2 min. The purple solution was added into 18.5 mL of 4 mg mL$^{-1}$ GO aqueous dispersion dropwise and stirred for 30 min to obtain the homogeneous dispersion. Then, 47.3 mg of Tp was added and the mixture was shaken for 20 min. The viscous liquid was transferred into an autoclave and heated at 120 °C for 24 h. After cooling down to room temperature, the obtained hydrogel was sequentially washed with water (2 × 30 mL), acetone (3 × 30 mL, soaking for 2 h each time), and water until acetone was replaced completely. After freeze-drying, the COF/RGO aerogel was obtained. For comparison, another three COF/RGO aerogels with different ratios of monomers and GO were also prepared under the same conditions, while only changing the mass of DB-SO$_3$H, NaOH, PTSA and Tp to 21.2 mg, 4.5 mg, 119 mg, 15.8 mg or 42.4 mg, 9.0 mg, 238 mg, 31.5 mg or 84.7 mg, 18.0 mg, 475 mg, 63.0 mg, respectively (Table S1). The obtained COF/RGO aerogels are denoted as CGA-3.3, CGA-3.8 and CGA-5.5, respectively.

Table S1. Amount of reactants used for preparing the COF/RGO aerogels. The concentration of GO aqueous dispersion used in all experiments is 4.0 mg mL$^{-1}$.

| Samples  | DB-SO$_3$H | NaOH | H$_2$O | PTSA | GO   | Tp    |
|---------|------------|------|--------|------|------|------|
| CGA-3.3 | 21.2 mg    | 4.5 mg | 6.2 mL | 119 mg | 18.5 mL | 15.8 mg |
|         | (0.11 mmol) | (0.11 mmol) |       | (0.63 mmol) |       | (0.08 mmol) |
| CGA-3.8 | 42.4 mg    | 9.0 mg | 6.2 mL | 238 mg | 18.5 mL | 31.5 mg |
|         | (0.23 mmol) | (0.23 mmol) |       | (1.25 mmol) |       | (0.15 mmol) |
| CGA-4.6 | 63.6 mg    | 13.5 mg | 6.2 mL | 357 mg | 18.5 mL | 47.3 mg |
|         | (0.34 mmol) | (0.34 mmol) |       | (1.88 mmol) |       | (0.23 mmol) |
| CGA-5.5 | 84.7 mg    | 18.0 mg | 6.2 mL | 475 mg | 18.5 mL | 63.0 mg |
|         | (0.45 mmol) | (0.45 mmol) |       | (2.5 mmol) |       | (0.3 mmol) |
Synthesis of TpPa-COF and TpBD-COF. 0.45 mmol diamine monomer (48.7 mg Pa or 82.9 mg BD) and 2.5 mmol (475 mg) PTSA were dispersed into 4 mL deionized water by ultrasound. 0.3 mmol (63 mg) Tp was then added and shaken for 20 minutes. The mixture was transferred into an autoclave and kept in the oven at 120 °C for 2 days. The product was washed using water (2 × 30 mL) and subsequently by acetone using Soxhlet extraction, then dried overnight under vacuum at 80 °C.

1.4. Performance Measurement

1.4.1. Dye uptake kinetics
To study the uptake kinetics, 5 mg of samples were dispersed in 5 mL of aqueous solutions containing pollutants with an initial concentration of 20 mg L⁻¹. The solutions were then capped and placed on an orbital shaker at 250 rpm for a given time (0.5 to 120 min). Afterwards, the samples were separated from the solutions and filtered through a 0.2 μm hydrophilic Nylon syringe filter to remove all the suspended samples. The resulting solutions were then analyzed by UV-visible spectroscopy at the specified wavelengths (663 nm for MB, 590 nm for CV and 554 nm for RhB, respectively) to determine the residual dye concentration in solution at each time point.

1.4.2. Dye uptake isotherms
To measure the maximum capacities of samples, the following experiments were performed. 5 mg of samples were added to 5 mL of an aqueous dye stock solution with an initial concentration of 20, 50, 100, 300, 600, or 900 mg L⁻¹. All samples were then capped and placed on an orbital shaker at 250 rpm for 2 days to ensure that equilibrium was reached. Afterwards, the samples were separated from the solutions and filtered through a 0.2 μm hydrophilic Nylon syringe filter to remove all the suspended samples. The resulting solution was then measured by UV-visible spectroscopy at the specified wavelengths to determine the residual dye concentration in solution at each dye concentration. This experiment was repeated three times with each sample.

1.4.3. Sample calculations and Langmuir fit for dye uptake isotherms
Dye removal efficiency (Removal (%)) and equilibrium adsorption capacity (qₑ) were
calculated by the following equations:

\[
\text{Removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100
\]

\[
q_e = \frac{C_0 - C_e}{m} \times V
\]

where \(C_0\) and \(C_t\) is the initial dye concentration and residual dye concentration in solution at time \(t\) (mg L\(^{-1}\)), respectively, \(q_e\) is the amount of dye adsorbed by the adsorbent at equilibrium (mg g\(^{-1}\)), \(C_e\) is the residual dye concentration in solution at equilibrium (mg L\(^{-1}\)), \(m\) is the mass of adsorbent (g), and \(V\) is the volume of the dye solution (mL).

The adsorption isotherms were analyzed by applying Langmuir isotherm model.\(^3\,^4\) The Langmuir isotherm model was expressed according to the following equation:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}
\]

where \(q_m\) is the maximum adsorption capacity of adsorbent (mg g\(^{-1}\)) and \(K_L\) is the Langmuir constant (L mg\(^{-1}\)). By fitting each isotherm with this model, values of \(q_m\) and \(K_L\) were obtained for each adsorbent/dye pair (Table S4).

1.4.4. pH effect and reusability investigation

To evaluate the pH effect, RhB aqueous solution (75 mg L\(^{-1}\)) was adjusted with 0.1 M NaOH or 0.1 M HCl in the pH range from 1 to 11. Then, 5 mg of CGA was dispersed in 5 mL of RhB aqueous solutions with different pH. After 60 min of adsorption, the sample was separated from the solutions and filtered through a 0.2 μm hydrophilic Nylon syringe filter to remove all the suspended samples. The resulting solutions were then analyzed by UV-visible spectroscopy to determine the residual dye concentration in solution.

The reusability experiment of dye adsorption was conducted with 10 mg of CGA in 10 mL of RhB solution (75 mg L\(^{-1}\)). After adsorption, the CGA was washed with acetone and water to desorb RhB from CGA and then freeze-dried for reusability tests.

1.4.5. Adsorption of anionic dyes

5 mg of CGA-4.6 was added to 5 mL of an aqueous dye stock solution (CR or MO) with an initial concentration of 300 mg L\(^{-1}\). The samples were placed on an orbital shaker for 24 hours to ensure that equilibrium was reached. Afterwards, the samples were separated from the solutions and filtered through a 0.2 μm hydrophilic Nylon syringe filter to
remove all the suspended samples. The resulting solution was then analyzed by UV-visible spectroscopy at the specified wavelengths to determine the residual dye concentration in solution.

1.4.6. COFs without charged groups

5 mg of TpPa-COF or TpBD-COF was added to 5 mL of RhB aqueous solutions (300 mg L\(^{-1}\)). The samples were placed on an orbital shaker for 24 hours to ensure that equilibrium was reached. Afterwards, the samples were separated from the solutions and filtered through a 0.2 μm hydrophilic Nylon syringe filter to remove all the suspended samples. The resulting solutions were then analyzed by UV-visible spectroscopy to determine the residual dye concentration in solution.
2. Results and Discussion (Supporting Figures and Tables)

Figure S1. Illustration of the synthesis of (a) COF-SO$_3$Na and (b) CGA via the hydrothermal method.

Figure S2. Powder XRD patterns of COF-SO$_3$Na after the material was immersed in different solvents for 2 days.
Figure S3. (a) N\textsubscript{2} adsorption-desorption isotherms (-196 °C) and (b) QSDFT pore size distribution of COF-SO\textsubscript{3}Na.

Figure S4. BET specific surface area plot for the N\textsubscript{2} sorption isotherm of COF-SO\textsubscript{3}Na.
Figure S5. SEM image and the corresponding elemental mapping images of COF-SO₃Na.

Figure S6. C 1s XPS spectra of (a) GO and (b) RGO.

Figure S7. STEM image and the corresponding elemental mapping images of CGA.
Figure S8. AFM image (left) and the corresponding height profiles (right) for RGO.

Figure S9. AFM image (left) and the corresponding height profile (right) for CGA-3.3.

Figure S10. AFM image (left) and the corresponding height profiles (right) for CGA-3.8.
Figure S11. AFM images (top) and the corresponding height profiles (bottom) for CGA-5.5.

Figure S12. (a) Photographs, (b) wide-angle XRD patterns and (c) FT-IR spectra of COF/RGO aerogels with different sheet thicknesses.
Figure S13. SEM images of (a, b) RGO, (c, d) CGA-3.3, (e, f) CGA-3.8, and (g, h) CGA-5.5.

Figure S14. N₂ adsorption-desorption isotherms (-196 °C) for (a) CGA-3.3, (b) CGA-3.8, (c) CGA-4.6, (d) CGA-5.5, and (e) RGO.
Figure S15. BET specific surface area plots for the N$_2$ sorption isotherms of (a) CGA-3.3, (b) CGA-3.8, (c) CGA-4.6, (d) CGA-5.5, and (e) RGO.
All the samples showed three-stage weight loss. The first weight loss (30–120 °C) is related to the evaporation of adsorbed water. The second weight loss in the range of 200–350 °C originates from the disintegration of functional groups, i.e., sulfonic groups for COF and oxygen-containing groups for RGO. The third one (> 350 °C) results from the decomposition of the COF backbone and some unstable carbon species removed from the skeleton of RGO. These weight loss processes agree with reported results. The thermal stability of CGAs is lower compared with RGO and gradually decreases with the increase of COF loading. The total mass losses are recorded to be 26.4, 28.1, 34.8, 41.8, 51.5 and 79.5 wt% for RGO, CGA-3.3, CGA-4.6, CGA-5.5, and COF, respectively.
Figure S17. Zeta potential values of RGO, COF and CGAs with different sheet thicknesses.
Figure S18. Adsorption kinetics of (a) MB, (b) CV and (c) RhB on CGAs with different sheet thicknesses. Adsorption isotherms and associated Langmuir fits of (d) MB, (e) CV, and (f) RhB on CGAs with different sheet thicknesses.

Figure S19. UV-vis absorption spectra of aqueous solutions of MB dye in the presence of (a) COF, (b) RGO, (c) CGA-3.3, (d) CGA-3.8, (e) CGA-4.6, and (f) CGA-5.5.
Figure S20. UV-vis absorption spectra of aqueous solutions of CV dye in the presence of (a) COF, (b) RGO, (c) CGA-3.3, (d) CGA-3.8, (e) CGA-4.6, and (f) CGA-5.5.

Figure S21. UV-vis absorption spectra of aqueous solutions of RhB dye in the presence of (a) COF, (b) RGO, (c) CGA-3.3, (d) CGA-3.8, (e) CGA-4.6, and (f) CGA-5.5.
Figure S22. Adsorption kinetics of RhB on COF powder.

Figure S23. (a) Removal efficiency of RhB with CGA at different pH values. (b) UV-vis absorption spectra of aqueous solutions of the RhB dye in the presence of CGA at different pH values. (c) Recyclability test of CGA for the adsorption of RhB. (d) Photographs of the RhB solution at initial concentration ($C_0$) and after 5 cycles. The initial concentration of RhB was 75 mg L$^{-1}$. 
The details of density functional theory (DFT) calculations

All DFT calculations were carried out by Gaussian 09 program (Revision D.01). The B3LYP functional by evaluation of dispersion (Grimme’s D3 dispersion correction) in combination with 6-31+G(d,p) basis set were used for the structure optimization of RhB+COF/graphene interface, and the subsequent calculation of frequency at the same level was performed to determine each binding site of ion-pair being indeed the minima on the potential energy surface. Then, the binding energy of COF/graphene and RhB was estimated by $E_b = E_b(A_B) - E_b(A) - E_b(B)$ where $E_b(A_B)$ stands for the energy of the interface, $E_b(A)$ and $E_b(B)$ represent for the energy of isolated species with the geometry in the optimized A_B structure. Moreover, to clarify the interaction mode between COF and RhB, the intermolecular H-bond energy ($E_{HB} = -223.08\rho_{BCP} + 0.7423$) was calculated by quantum theory of atoms in molecules (QTAIM). QTAIM is a well-known theoretical tool to reveal inter- and intramolecular interactions, within QTAIM, the electron density as well as other real space functions such as energy density and the Laplacian of electron density at the so-called bond critical point (BCP) of the H-bond interaction of interest can be comprehensively analyzed. To visualize the weak intermolecular interactions intuitively, the noncovalent interaction (NCI) analysis, which is also known as the reduced density gradient (RDG) method, was conducted. This method is a very popular method for studying weak interaction. All of the calculations of BCP and NCI analysis were completed by Multiwfn code.

The RhB+COF/graphene interface construction

To detect the interactions between COF, RhB, and graphene, the simplified model of RhB+COF/graphene based on the interface (labels in orange in Figure S24a, b) was constructed to provide a preliminary understanding. Accordingly, the two conformations determined by the relative orientation between RhB and COF were considered based on the hydrogen bonding (H-bond) modes: for the Conformation-1, the Cl of RhB is orientated to the H attached to the N of COF backbone; for the Conformation-2, the H of -COOH in RhB is oriented to the O of -SO$_3$ attached to the benzene of COF (see the location highlighted in blue box in Figure S25). The reason for the construction of these
two conformations can be ascribed to the fact that the N-H site of COF is a strong H-bond donor, which interacts with Cl strongly, and the -SO\textsubscript{3} site of COF is a strong H-bond acceptor, interacting with the -COOH site of RhB mostly. This phenomenon has been observed in ionic liquids with abundant H-bond donor-acceptor sites.\textsuperscript{14-16} Notably, the edge C atoms of graphene have been saturated with H atoms.

Figure S24. The representation of RhB+COF/graphene interface: (a) the top view and (b) the side view (the red, blue, and grey represent for RhB, COF, and graphene, respectively. The region in orange box is the real structure for DFT calculations).
Figure S25. The orientation of COF and RhB in the (a) Conformation-1 and (b) Conformation-2 (the location of H-bonding is highlighted in blue box, the graphene is displayed by line mode, the COF and RhB are displayed by ball and stick mode, and the C atoms of RhB and COF are shown for clarity in brown and dark green, respectively).
Figure S26. Conformation-1 of RhB+COF/graphene: (a) the top view, (b) the side view, and (c) the H-bonding interaction between RhB and COF (the value shows the H-bond distance in Å, the graphene is displayed by line mode, the COF and RhB are displayed by ball and stick mode, and the C atoms of RhB and COF are shown for clarity in brown and dark green, respectively).
Figure S27. Conformation-2 of RhB+COF/graphene: (a) the top view, (b) the side view, and (c) the H-bond interaction between RhB and COF (the value shows the H-bond distance in Å, the graphene is displayed by line mode, the COF and RhB are displayed by ball and stick mode, and the C atoms of RhB and COF are shown for clarity in brown and dark green, respectively).
Figure S28. The color-filled reduced density gradient (RDG) isosurface map of critical H-bond sites of Conformation-1 (a-c) and Conformation-2 (d-f). The red, blue, and green represent steric effect that exists within the aromatic ring, strong H-bond, and van der Waals interaction, respectively (the values in picture are the H-bond energy unit in kcal mol$^{-1}$).
Figure S29. (a) Chemical structures of MO and CR. (b) Adsorption of anionic and cationic dyes on CGA at an initial dye concentration of 300 mg L$^{-1}$. 
Figure S30. (a) Pore structure, (b) powder XRD pattern, and (c) N$_2$ sorption isotherm (-196 °C) of TpPa-COF. (d) Pore structure, (e) powder XRD pattern, and (f) N$_2$ sorption isotherm (-196 °C) of TpBD-COF. The insets in (c) and (f) are BET specific surface area plots of TpPa-COF and TpBD-COF, respectively. The correlation coefficient and C constant are given in Table S3.

Figure S31. Adsorption of RhB (initial dye concentration of 300 mg L$^{-1}$) on TpPa-COF, TpBD-COF, and COF-SO$_3$Na.
Table S2. Experimental element analysis (wt%) results for all the samples, the calculated COF loading amount (wt%) in hybrid aerogels, and theoretical element content (wt%) of COF.

| Samples   | C%  | H%  | N%  | S%  | COF loading based on N | COF loading based on S |
|-----------|-----|-----|-----|-----|------------------------|------------------------|
| RGO       | 73.71 | 0.90 | 0.00 | 0.00 |                        |                        |
| CGA-3.3   | 67.38 | 2.06 | 3.54 | 2.03 | 49.4%                  | 35.7%                  |
| CGA-3.8   | 64.32 | 2.51 | 3.75 | 2.69 | 52.3%                  | 47.4%                  |
| CGA-4.6   | 58.29 | 2.81 | 4.58 | 3.67 | 63.9%                  | 64.6%                  |
| CGA-5.5   | 60.63 | 2.46 | 4.83 | 3.81 | 67.4%                  | 67.1%                  |
| COF-SO₃Na | 46.94 | 4.51 | 7.17 | 5.68 |                        |                        |

Theoretical element content of COF 45.87 2.25 8.91 10.20

The experimental elemental analysis of H% for COF is higher than the theoretical one and this can be attributed to its hygroscopic nature, which is also observed from the TGA data (Figure S16). The initial weight loss of COF before 120 °C is attributed to the adsorbed water. The experimental value of S% is lower than the theoretical one possibly because a small portion of sulfonate groups is removed during the hydrothermal process.
Table S3. BET specific surface area ($S_{BET}$), correlation coefficient, C constant, pore volume, and density of all the samples.

| Samples   | $S_{BET}$ (m$^2$ g$^{-1}$) | Correlation coefficient | C constant | Pore volume (cm$^3$ g$^{-1}$) | Density (mg cm$^{-3}$) |
|-----------|---------------------------|-------------------------|------------|-------------------------------|------------------------|
| COF-SO$_3$Na | 179                       | 0.9999                  | 76.387     | 0.240                         | ~102                   |
| CGA-3.3   | 149                       | 0.9999                  | 119.129    | 0.241                         | 10.6                   |
| CGA-3.8   | 159                       | 0.9999                  | 140.698    | 0.256                         | 7.4                    |
| CGA-4.6   | 185                       | 0.9999                  | 150.449    | 0.338                         | 7.1                    |
| CGA-5.5   | 169                       | 0.9999                  | 343.385    | 0.239                         | 10.2                   |
| RGO       | 114                       | 0.9999                  | 67.783     | 0.202                         | 15.8                   |
| TpPa-COF  | 805                       | 0.9999                  | 771.409    | 0.638                         |                        |
| TpBD-COF  | 686                       | 0.9989                  | 89.749     | 0.437                         |                        |
Table S4. Summary of adsorption capacity ($q_m$) and affinity ($K_L$) values obtained from the Langmuir fit of the isotherms.

| Samples | RhB | CV | MB |
|---------|-----|----|----|
|         | $q_m$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) | $q_m$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) | $q_m$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) |
| COF     | 130 | 1.25 | 178 | 6.06 | 308 | 2.39 |
| CGA-3.3 | 276 | 0.37 | 230 | 0.08 | 299 | 1.72 |
| CGA-3.8 | 299 | 0.86 | 308 | 3.07 | 288 | 2.98 |
| CGA-4.6 | 368 | 1.31 | 328 | 3.83 | 334 | 2.89 |
| CGA-5.5 | 322 | 0.07 | 315 | 3.39 | 330 | 2.39 |
| RGO     | 157 | 0.03 | 129 | 4.33 | 211 | 1.87 |
3. Supporting references

1. Y. Xu, K. Sheng, C. Li, G. Shi, *ACS Nano* 2010, 4, 4324–4330.

2. C. Li, J. Yang, P. Pachfule, S. Li, M.-Y. Ye, J. Schmidt, A. Thomas, *Nat. Commun* 2020, 11, 4712.

3. B. Dong, W.-J. Wang, S.-C. Xi, D.-Y. Wan, R. Wang, *Chem. Eur. J.* 2021, 27, 2692–2698.

4. Y. Li, C.-X. Yang, H.-L. Qian, X. Zhao, X.-P. Yan, *ACS Applied Nano Materials* 2019, 2, 7290–7298.

5. S. Chandra, T. Kundu, K. Dey, M. Addicoat, T. Heine, R. Banerjee, *Chem. Mater.* 2016, 28, 1489–1494.

6. T. Wu, X. Wang, H. Qiu, J. Gao, W. Wang, Y. Liu, *J. Mater. Chem.* 2012, 22, 4772.

7. M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta Jr., F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D.01, Wallingford Ct, Gaussian Inc., 2013.

8. S. Grimme, *J. Comput. Chem.* 2004, 25, 1463-73.

9. S. Emamian, T. Lu, H. Kruse, H. Emamian, *J. Comput. Chem.* 2019, 40, 2868-2881.

10. R. W. F. Bader, *Atoms in Molecules: A Quantum Theory. Oxford University Press, New York*, 1990.

11. E. R. Johnson, S. Keinan, P. Mori-Sanchez, J. Contreras-Garcia, A. J. Cohen, W. Yang, *J. Am. Chem. Soc.* 2010, 132, 6498-506.
12. T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580-92.

13. Http://Sobereva.com/Multiwfn/.

14. K. S. Egorova, E. G. Gordeev, V. P. Ananikov, *Chem. Rev.* **2017**, *117*, 7132-7189.

15. P. A. Hunt, C. R. Ashworth, R. P. Matthews, *Chem. Soc. Rev.* **2015**, *44*, 1257-88.

16. O. Nordness, J. F. Brennecke, *Chem. Rev.* **2020**, *120*, 12873-12902.