Surfactant-assisted lamellar structuration of tunable Co-based hybrid nanosheets

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Figure S1: SEM images of Co-160-BDC-Oam
Determination of specific surface by SAXS:

The specific surface of the materials were calculated from the Porod region and the Porod’s law (eq. 1)

\[
\lim_{q \to \infty} I(q) = 2\pi(\Delta \rho)^2 \Sigma \frac{1}{q^4}
\]

eq. 1

With \( \Delta \rho \) the scattering length density difference between the material and air and \( \Sigma \) the surface in the probed volume, i.e. the \( \frac{S}{V} \) with \( S \) the surface area of the sample and \( V \) the volume of the sample probed.

To easily obtained \( \frac{S}{V} \), the scattering intensities of the various samples were plotted as eq. 2:

\[
Iq^4 = 2\pi(\Delta \rho)^2 \frac{S}{V} + Bq^4
\]

eq. 2

With \( B \) the background scattering of the patterns. The results are presented on Figure S 2-S 3.

Figure S 2: Porod plot of the scattering intensities of Co-160-BDC-Oam (black dot), Co-220-BDC-hexylamine (green dot) and fitting line (black line)
Then, $S$ was calculated from the intercept of the linear fit of the Porod region considering that all materials have a mass density and a composition close to the one of Co-160-BDC-OAm ($\rho_m = 1.6 \text{ g.cm}^{-3}$). The results obtained are presented in the Table SIX.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$S$ (m$^2$.g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-160-BDC-OAm</td>
<td>$33.5 \pm 2$</td>
</tr>
<tr>
<td>Others</td>
<td>$27.4 \pm 2$</td>
</tr>
</tbody>
</table>

*Figure S3: Porod plot of the scattering intensities of Co-190-BDC-Oam (red dot), Co-220-BDC-Oam (blue dot), Co-220-BDC-hexadecylamine (orange dot) and fitting line (black line)*
Figure S4: isotherme adsorption of Co-16O-BDC-Oam
**TEM and Image treatment:**

ImageJ software was used for treatment. In order to measure the distances between two dark fringes ($d_{Co-Co}$), the TEM images (A) are subjected to a Fourier transform (on red square). This Fourier transform (B) is used to create a filter (C) by thresholding the FT which highlight the selected repetitive patterns (D). The gray value of C image was inverted to better distinguish the before and after thresholding. This allows for a better definition of the gray shades. Plot E shows the gray scale values along the blue arrow in image D. The uncertainty indicates the size of a pixel (0.2nm). The same process is applied for all the following figures S5-S12:

*Figure S 5: Co-160-BDC-Oleylamine*
Figure S 6: Co-190-BDC-Oleylamine

Figure S 7: Co-220-BDC-Oleylamine
Figure S 8: Co-220-BDC-hexylamine

Figure S 9: Co-220-BDC-Hexadecylamine
Figure S10: Co-160-NDC-Oleylamine

Figure S11: Co-160-PDAA-Oleylamine
Figure S12: Co-160-BPDC-Oleylamine
FTIR:

Figure S 13: FTIR spectrum BDC
TGA-DTA

On the Figure S 11, the TGA-DTA analysis displays the mass loss of the material as a function of time and heat flow of the material during the analysis (this value is in arbitrary units and serves only to demonstrate the exo- and endothermic character of the mass losses). It should be noted that the thermal decomposition of the material occurs in several stages. Firstly, from 20°C to 200°C two very weak mass losses are observed which is characteristic of the evaporation of free and bound water molecules respectively. During the 300°C plateau, a particular mass loss in two steps is observed, composed of a weak loss during the first hour and a second fast important loss during the following half hour. These mass losses correspond to the combustion of the oleylamine and the linker, respectively, as suggested by the formation of nitrogenous species only in the first mass loss measured by mass spectrometry. Finally, during heat up to 400°C a last very weak mass loss occurs corresponding probably to the departure of residual carbon. (The mass ratio of the two mass losses at 300°C is about 15 BDC:Oam, which would correspond to a molar ratio of 25.)

![Figure S 14](image_url)
XPS analysis

The results of the XPS analysis confirm the presence of carbon, oxygen, nitrogen and cobalt atoms in the synthesized material. The decomposition of the signals corresponding to the 1s orbitals of the carbon, oxygen and nitrogen atoms corroborates the results previously presented concerning the chemical composition of the material. Indeed, the signal obtained for the 1s orbital of the oxygen atom is composed of three components: 531.7 eV (C-O), 533.1 eV (C=O) and 530.2 eV (O-Co). This result confirms the presence of carboxylate functions as well as the coordination with cobalt atoms. Similarly, the signal of the 1s orbital of the carbon atom is decomposed into three components: 288.0 eV (O-C=O), 284.8 eV (C-C/C=C) and 286.1 eV (C-N). The presence of the signal at 286.1 eV is characteristic of the presence of oleylamine molecules in the final material in agreement with the observations made in IR and DTA-TGA. The presence of oleylamine is also confirmed by the signal observed at 400.4 eV corresponding to the 1s orbital of the nitrogen atom of a primary amine.

![Figure S15: XPS spectrum of C 1s orbital (Black) with Gaussian fitting (red) composed with C-C/C=C (blue), C-OH (dark Green) O-C-O (bright Green) and baseline (orange)](image-url)
Figure S 16: XPS spectrum of O 1s orbital (Black) with Gaussian fitting (red) composed with C-O (blue), C=O (dark Green) and baseline (orange)

Figure S 17: XPS spectrum of N 1s orbital (Black)
Figure S 18: Scattering Intensities of Co-220-BDC-A with A=oleylamine (blue), A=hexylamine (green), A=hexadecylamine (orange) and A=tetradecylamine (purple)
Modification of linker

Figure S 19: FTIR spectrum of Co-160-BDC-Oam (black), Co-160-NDC-Oam (red), Co-160-PDAA-Oam (blue) and Co-160-BPDC-Oam (green)
Figure S20: Powder X-ray diffractograms of Co-160-BDC-Oam (black), Co-160-NDC-Oam (red), Co-160-PDAA-Oam (blue) and Co-160-BPDC-Oam (green)
Determination of angular deviation

The angular deviation (α) is calculated with the equation 3:

\[ \alpha = \cos^{-1} \left( \frac{\text{PXRD value}}{\text{DFT value}} \right) \]

\text{eq. 3}

Figure S21: illustration of angular deviation
Modification of amine for NDC ligand

Figure S 22: Scattering Intensities of Co-220-NDC-A with $A=\text{oleylamine}$ (blue), $A=\text{hexylamine}$ (green) and $A=\text{hexadecylamine}$ (orange)