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Arylamine-Linked Covalent Organic Frameworks for Efficient Pseudocapacitive Energy Storage

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Abstract: Developing new linkages is one of the most efficient strategies to enrich the diversity of covalent organic frameworks (COFs). Particularly, functional linkages can endow COFs with additional tailored properties besides the building units, which thereby further diversify COFs with desired functions. Herein, for the first time. we developed a new arylamine linkage for the construction of COFs. Two new arylamine-linked COFs (AAm-TPB and AAm-Py) were prepared by condensing cost-effective dimethyl succinvl succinate (DMSS) with corresponding multitopic amines (TPB-NH₂ and Py-NH₂). Due to the abundant electroactive diphenylamine moieties in the COF skeletons resembling that of polyaniline (PANI), one of the state-ofthe-art conductive polymer, the pseudocapacitive energy storage performance of AAm-TPB was further investigated. Remarkably, AAm-TPB electrode exhibits a high capacitance of 271 F g⁻¹ with a three-electrode setup at a discharge rate of 1 A g⁻¹, which represents one of the highest capacitances among the reported COF-based electrode materials.

Covalent organic frameworks (COFs) as an emerging class of crystalline porous polymers have spurred increasing research interests and manifested promising applications¹ including gas storage and separation,² catalysis,³ energy storage,⁴ sensors,⁵ and among others.⁶ COFs are generally comprised of organic knots and suitable linkages, in which linkages play extremely important roles in connecting organic building blocks into crystalline networks. It is well accepted that reversible linkages facilitate the formation of crystalline networks. Thus, extensive research efforts have been devoted to boronic ester and boroxine,⁷ imine groups and related linkages formed by reversible reactions.8 Remarkably, linkages with less reversibility such as olefin and dioxin have also been utilized to construct COFs which not only exhibit ultrastability but also show promising optoelectronic properties.9 Recently, ester-linked COFs were synthesized via transesterification reactions which led to a crystalline hexagonal COF with the largest edge length.¹⁰ Besides, aminal-linkage were demonstrated to render the formation of crystalline networks which showed similar photophysical properties as those of the monomers.¹¹ In addition, higher valency COFs with B-O-P linkages were reported very recently, which may greatly increase the structure types for COFs.12 With the evolution of these newly developed linkages, the scope of COFs was considerably expanded. Meanwhile, the diversity of linkages also confers COFs with additional fascinating properties. Hence, exploring new linkages is essential to expand the family of COFs and their potential applications. However, developing new linkages for COF synthesis remains challenging.

The condensation between dimethyl succinyl succinate (DMSS) and amine derivatives was widely used for synthesizing quinacridone and its derivatives.¹³ Recently, Fang et al. developed several ladder-type polyaniline-analogous polymers this condensation. which exhibited excellent usina electrochemical properties.14 The reaction mechanism is shown in Scheme 1a, which is similar to imine condensation.¹⁵ This condensation is reversible, and thus is beneficial for COF synthesis. Different from the aliphatic amine linkage (-CH₂-NH-) reported by Deng,8f Lotsch,16 Ma17 and Zhao11 (Chart 1), the arylamine linkage (-NH-) developed herein not only feature improved stability but also maintain high conjugation degree beneficial for electrical conduction and redox activity. Moreover, the diphenylamine moieties generated by this condensation is resembling to the repeating units of polyaniline (PANI), which may further confer the unprecedented arylamine-linked COFs with many promising applications.¹⁸ Taking these into considerations, we designed and synthesized two arylamine-linked twodimensional (2D) COFs, which as far as we know, represent the first two arylamine-linked COFs. Furthermore, these arylaminelinked COFs were applied in energy storage with superior performance compared to those of the imine-linked COF analogues (Figure 3b and S29).

To demonstrate the feasibility of arylamine-linked COF synthesis, we firstly synthesized the model compound (DATP) by *p*-toluenesulfonic acid (PTSA)-catalyzed condensation of commercially available and cost-effective DMSS and aniline





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Scheme 1. Reaction mechanism and synthetic routes for model compound DATP and arylamine-linked COFs. Inset shows photographs of DAHC and DATP under ambient donditions.

followed by oxidation in air. (Scheme 1b). The successful synthesis of DATP and intermediate compound DAHC were confirmed by nuclear magnetic resonance (NMR) spectroscopy and single crystal X-ray diffraction analysis (Figure S21 and Figure S36-39). Then, DMSS was further utilized to react with different multitopic amine monomers of 1,3,5-tris(4aminophenyl)benzene (TPB-NH₂) and 4,4',4",4"'-(pyrene-1,3,6,8tetrayl)tetraaniline (Py-NH₂) to afford the arylamine-linked COFs with different topologies (hcb for AAm-TPB and sql for AAm-Py, Scheme 1c). The reaction was performed under solvothermal condition at 120 °C for 3 days catalyzed by PTSA followed by oxidation in O₂ atmosphere. Both COFs were obtained as insoluble red or orange powders in high yields (84% and 83% for AAm-TPB and AAm-Py, respectively).

The chemical structures of both COFs were confirmed by Fourier transform infrared (FT-IR) and solid-state ¹³C Cross-Polarization with total suppression of spinning sidebands (CP-TOSS) spectroscopies. The FT-IR spectra and ¹³C NMR spectra of the arylamine-linked COFs were quite similar to those of the model compound DATP, which suggests the similar structural compositions between DATP and the COFs. As for the FT-IR spectra (Figure 1c and S1), both the characteristic N-H stretching bands (3470 and 3420 cm⁻¹ for TPB-NH₂, 3426 and 3326 cm⁻¹ for Py-NH₂) from amine monomers and C=O stretching mode (1631 cm⁻¹) from DMSS were disappeared in both COFs, which suggested the high condensation efficiency. Additionally, the disappearances of the C-N stretching (1609 cm⁻¹ for TPB-NH₂ and 1613 cm⁻¹ for Py-NH₂) from the amine monomers and the appearances of new stretching (1525 cm⁻¹ for AAm-TPB and 1512 cm⁻¹ for AAm-Py) for both COFs indicated the formation of secondary amines with new C-N single bonds. Furthermore, compared with reported imine COFs, the peaks of C=N imine moieties are absent in both AAm-TPB and AAm-Py, suggesting no imine formation in both COFs, which is also confirmed by the FT-IR and ¹³C CP-TOSS NMR spectra (Figure S2 and S10). The solid-state diffuse reflectance UV-vis spectra suggest both arylamine-linked COFs exhibited featureless and broad absorption ranging from 300 to 800 nm (Figure 1d). In contrast, the imine-linked COF analogues showcased much narrower and blue-shifted absorption than the arylamine-linked COFs (Figure S3). The large bathochromic shifts of ca. 135 and 86 nm on the absorption onset of the arylamine-linked COFs compared to their imine-linked COF counterparts clearly indicate much improved conjugation and narrower optical bandgaps (1.96 eV for AAm-TPB and 1.97 eV for AAm-Py) among the arylamine-linked COFs than those of imine-linked ones (2.53 eV for TPB-TP-COF^{19a} and 2.31 eV for Py-1P COF^{19b}, Figure S4). This result further demonstrates better electron delocalization in the arylamine-linked COFs.

The crystalline structures of arylamine-linked COFs (AAm-TPB and AAm-Py) were examined by powder X-ray diffraction (PXRD) measurement. The PXRD patterns simulated by Materials Studio suggested that both AAm-TPB and AAm-Py fitted well with the corresponding eclipsed AA-stacking modes (Figure 2, S18 and S19). Intriguingly, the refined structures of arylamine-linked COFs are closely similar to those of imine-linked COFs analogues.¹⁹ The permanent porosities of both arylaminelinked COFs were assessed by nitrogen sorption measurements at 77 K. The nitrogen adsorption isotherm of AAm-TPB exhibits typical type-IV characteristics, which indicates its mesoporous character (Figure 1b). In sharp contrast, AAm-Py features a type-I isotherm, suggesting its microporous characteristics (Figure S5). AAm-TPB revealed a Brunauer-Emmett-Teller (BET) surface area of 403 m² g⁻¹, calculated from the N₂ adsorption isotherm in the pressure region of $P/P_0 < 0.15$. The BET surface of AAm-Py was determined as 285 $m^2\ g^{\text{-1}}$ by the same method. Such moderate BET surface area might be ascribed to the unfavorable interactions between the skeleton and guest gas molecules,16a trapped oligomers in the channels, and possible structural defects. This phenomenon has also been observed in other COFs (Table

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Figure 1. (a) Comparison of solid state ¹³C CP/TOSS NMR of AAm-TPB and solution ¹³C NMR spectra of DAHC and DATP reference. Asterisks indicate residual *n*-butanol. (b) N₂ adsorption-desorption isotherms (77 K) and pore-size distribution of AAm-TPB. (c) FT-IR spectra of DMSS, TPB-NH₂, DATP and AAm-TPB. (d) The solid-state diffuse reflectance UV-vis absorption spectra of TPB-TP-COF, Py-1P COF, AAm-TPB and AAm-Py. Inset shows photographs of AAm-TPB, AAm-Py, TPB-TP-COF, Py-1P COF, Py

S1) containing the linkages of "-NH-".^{81,8g,16-17} The pore volume of AAm-TPB and AAm-Py were 0.32 and 0.43 cm³ g⁻¹ ($P/P_0 = 0.99$), respectively. Pore size distributions (PSDs) based on the nonlocal density functional theory (NLDFT) method showed the dominant pore sizes for AAm-TPB and AAm-Py were 2.99 nm and 1.02 nm, respectively (Figure 1b and S5), both of which agreed well with the theoretical values (3.01 nm for AAm-TPB and 1.09 nm for AAm-Py, Figure 2b and 2d). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the morphologies of both arylamine-linked COFs. SEM images showed AAm-TPB was composed of spheres, while AAm-Py showcased a fibrillar morphology (Figure S12). Moreover, TEM images of both arylamine-linked COFs disclosed clear lattice stripes, further indicating the long-range ordering structures of these COFs (Figure S13).

Thermogravimetric analysis (TGA) measurement was employed to evaluate the thermal stability of the two arylaminelinked COFs. As displayed in Figure S14, both arylamine-linked COFs showcased moderate thermostability and exhibited weight loss started at around 240 °C, which was comparable to that of PANI.²⁰ AAm-Py retained 77% of the initial mass, and the mass decreased to 60% for AAm-TPB at 800°C under N₂ atmosphere. Additionally, the chemical stability of both AAm-TPB and AAm-Py were tested by soaking the powder in 1 M H₂SO₄, 6 M HCl and 6 M NaOH aqueous solutions at room temperature for 24 h, respectively. Both AAm-TPB and AAm-Py maintained the crystallinity, porosity and chemical composition under all aforementioned conditions after characterization by PXRD, N₂ sorption and FT-IR profiles, which indicated the high stability of the arylamine-linked COFs in these harsh conditions (ESI, Section 9).

PANI as a well-known electrically conductive polymer has been extensively utilized to fabricate electrodes for supercapacitors.²¹ Bearing similar arylamine linkages in the backbone as that in PANI, the supercapacitor performance of AAm-TPB was thus investigated. The electrochemical behaviors of AAm-TPB were first studied in 1.0 M H_2SO_4 using a three-electrode setup. As presented in Figure 3a, AAm-TPB-based electrode displayed two pairs of reversible redox peaks at 0.82/0.67 V and 0.48/0.41 V (vs Ag/AgCI) at a scan rate of 1 mV s⁻¹, respectively, which indicated a quasi-reversible redox process. A possible redox process was proposed in the Supporting Information (Section 15), which involved transitions



Figure 2. (a) Experimental and refined PXRD patterns of AAm-TPB, difference plot of experimental and refined PXRD pattern. (b) Top-view and side-view for AA stacking model of AAm-TPB. (c) Experimental and refined PXRD patterns of AAm-Py, difference plot of experimental and refined PXRD pattern. (d) Top-view and side-view for AA stacking model of AAm-Py.

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Figure 3. (a) CV curve of AAm-TPB at 1 mV s⁻¹. (b) GCD curves of AAm-TPB at different current densities. (c) The Nyquist plots of AAm-TPB. (d) The long-term cycle test of AAm-TPB at a current density of 5 A g⁻¹. Inset: GCD profiles of AAm-TPB in the first and last 6 cycles. (e) Energy density and power density of the AAm-TPB//AC device using two-electrode system. Inset: a red light-emitting diode (1.8 V) lit by AAm-TPB//AC cells. (f) Gravimetric capacitance of AAm-TPB dependence on different scan rates.

from benzoid diamine to quinoid diimine and from enol to ketone.²¹ In addition, the cyclic voltammetry (CV) curves at different scan rates (1 to 200 mV s⁻¹) between 0.2 and 0.9 V remained symmetrical, which demonstrated excellent electrochemical reversibility and distinct capacitive behaviors even at high scan rates (Figure S24). Galvanostatic chargedischarge (GCD) measurements were further carried out to evaluate the capacitance of AAm-TPB-based electrode. AAm-TPB showed a symmetrical GCD curve with two plateaus at ~0.7 V and ~0.4 V, which was consistent with the redox peaks of the CV curves (Figure 3b). And a high gravimetric capacitance of 271 F g^{-1} was achieved at the current density of 1 A g^{-1} (Figure 3f). Notably, AAm-TPB retained a high capacitance of 201 F g⁻¹ even when the current density was increased to 10 A g⁻¹, which outperformed most reported COF-based electrode materials (Figure 3b and S25, Table S6).

Electrochemical impedance spectroscopy (EIS) measurement was performed to evaluate the diffusion resistance of AAm-TPBbased electrode. As shown in Figure 3c, the Nyquist plot indicated lower charge transfer resistance and ionic diffusion resistance between AAm-TPB-based electrode and the electrolyte. Moreover, the long-term cycling test of AAm-TPB-based electrode showed good electrochemical durability with 91% capacitance retention after 10,000 cycles at 5 A g⁻¹ (Figure 3d). CV, GCD and EIS measurements were performed again after the long-term cycling, no significant difference was observed, which indicated exceptional long-term cyclability of AAm-TPB-based electrode (Figure S26). Such superior cyclability might be ascribed to the intralayer hydrogen bonding, which not only confers arylamine-linked COFs with the comparatively high stability of both oxidation and reduction states during the electrochemical process, but also improve the electron transfer kinetics.²² The existence of intralayer N-H···O H-bonding [D =2.667 Å, d = 1.818 Å, $\theta = 135.99^{\circ}$] between arylamine N-H and the carbonyl 'O' in AAm-TPB was suggested from similar hydrogen bonding [D = 2.690 Å, d = 2.046 Å, $\theta = 131.00^{\circ}$] observed in the crystal structure of DATP (CCDC: 2078875) and the same FT-IR spectra with DATP (ESI, Section 12).²³

To figure out the contributions of diphenylamine moieties and hydrogen bonding in the COF skeletons on the capacitance, the capacitances of two imine-linked COF analogues and commercial PANI were investigated by the same mothod. As demonstrated in Figure S28 and S29, neither TPB-DMTP-COF nor TPB-TP-COF shown any capacitative behaviour although TPB-DMTP-COF features a large BET surface area of 2190 m² g⁻¹. In constrast, PANI with a low BET surface area (36 m² g⁻¹, Figure S6) showcased a decent capacitance of 214 F g⁻¹ at 1 A g⁻¹ which confirmed the positive effect of diphenylamine moieties on the capacitance. While a high capacitance of 271 F g⁻¹ was obtained for AAm-TPB. As mentioned in possible redox process (ESI, Section 15), except the transformation from benzoid diamine to quinoid diimine, the intralayer hydrogen bonding are also conducive to improve the capacitance.²⁴

To further evaluate the electrochemical performance of AAm-TPB-based electrode, an asymmetric supercapacitor (ASC) of AAm-TPB//activated carbon (AC) was fabricated in a twoelectrode device with AAm-TPB as the anode material and AC as the cathode material. Subsequently, CV, GCD, EIS and long-term cyclability measurements were again performed on this AAm-TPB//AC device in the potential range of 0.2–0.9 V. Similar to the three-electrode setup measurement, the CV curves of AAm-TPB//AC device showed good electrochemical reversibility at different scanning rates (1–200 mV s⁻¹, Figure S30). The GCD profiles at different current densities from 1.0 to 20 A g⁻¹ were displayed in Figure S31 and a high capacitance of 281 F g⁻¹ at 1.0 A g⁻¹ was achieved. Notably, as shown in the Ragone plot (Figure 3e) and Table S7, the maximum energy density and power density of AAm-TPB//AC device were 19.16 W h kg⁻¹ and

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350 W kg⁻¹ at the current density of 1 A g⁻¹, respectively. In addition, the AAm-TPB//AC device still retained about 92% of the initial capacitance after 10,000 cycles under the current density of 5 A g⁻¹ (Figure S33). Moreover, three AAm-TPB//AC devices in series successfully lighten a 1.8 V LED (Figure 3e).

In summary, we developed a new arylamine linkage for the construction of COFs. The condensation of cost-effective DMSS and amine derivatives (TPB-NH₂ and Py-NH₂) afforded arylamine-linked COFs with **hcb** and **sql** topologies, respectively. These arylamine-linked COFs not only inherit superior stability as that of alkylamine-linked COFs, but also exhibit better conjugation than the alkylamine-linked COF counterparts, which would greatly expand the diversity of COF based electrode materials for electrochemical energy storage. In particular, AAm-TPB exhibited excellent capacitance up to 271 F g⁻¹ at 1 A g⁻¹. We envision that more arylamine-linked COFs will be explored in the near future on account of the specific functions of this arylamine linkage, which could further increase the application potentials of COFs.

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To expand the diversity of covalent organic frameworks (COFs) and explore their potential applications, for the first time, we developed a new arylamine linkage for construction of COFs. Due to the abundant electroactive diphenylamine moieties in the COF skeletons resembling that of polyaniline (PANI), AAm-TPB electrode demonstrates excellent performance in energy storage with a capacitance up to 271 F g^{-1} at 1 A g^{-1} .