Experimental details

Materials and methods
All procedures were performed under aerobic conditions. Solvents and reagents were obtained from commercial sources and used as received. Microanalyses (C, H, N) were performed with an EA 1108 Carlo Erba analyzer. IR spectra were recorded on a Shimadzu FT/IR IRAffinity-1 spectrometer with samples prepared as KBr pellets. TGA diagrams were recorded on a Mettler-Toledo TGA/DSC1 instrument under a N$_2$ flow of 50 ml/min. Powder XRD data were collected on freshly prepared samples on a PANalytical X’Pert Pro MPD diffractometer. $^1$H-NMR spectra were recorded on a Varian UNITY Plus spectrometer operating at 300 MHz. Samples were run in a 5 mm probe with D$_2$O or DMSO-d$_6$ as internal lock and reference. Energy-dispersive X-ray spectroscopy (EDS) analysis was performed with a scanning electron microscope with EDS spectroscopy.

X-ray crystallography
The data for the single crystal of Ca-MOF were collected on a Bruker SMART APEX II Duo CCD with Mo radiation from an IgS micro-focus source. A suitable crystal was mounted on a Hampton cryoloop with Paratone-N oil and transferred to a goniostat for data collection. Data integration and reduction were performed using SaintPlus 7.68A implemented in APEX2.$^1$ Absorption correction was performed by multi-scan method implemented in SADABS.$^2$ Space groups were determined using XPREP implemented in APEX2.$^1$ The structure was solved by direct methods using SHELXS-97$^3$ and refined by full-matrix least-squares techniques on $F^2$ with SHELXL-2014/7$^4$ contained in WinGX v2014.1 program package. The non-H atoms were treated anisotropically, whereas the aromatic and methyl H atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms.
Anodic stripping voltammetry (ASV)
The determination of Cu was performed with the ASV technique, using Trace Metal Analyzer (797 VA Computrace, Metrohm AG Ltd, Switzerland). More specifically, a three electrode system was used comprising Hanging Mercury Drop Electrode (HMDE) as working electrode, Platinum (Pt) as auxiliary electrode and Ag/AgCl/ KCl (3mol/L) as reference electrode. Prior the analysis, the solutions were appropriately diluted, so that the measuring concentrations to be <1 ppm. The analysis has been done following the AN-V-086 protocol developed by Metrohm (http://www.metrohm.com/en/applications/#).

ASV is extremely sensitive technique for metal analysis, capable of measuring a number of metals in concentrations down to $10^{-10}$ M. Actually, the sensitivity of ASV can be as good as that of ICP-MS analysis, using relatively inexpensive instrumentation (whereas ICP-MS instruments are rather expensive and consume large amount of Ar). The detection and quantification limits for Cu analysis achieved with ASV can be as low as 0.05-0.24 and 0.17-0.80 ppb respectively.

Electron Paramagnetic Resonance (EPR) spectroscopy
Electron Paramagnetic Resonance (EPR) spectra were recorded with a Bruker ER200D spectrometer at liquid nitrogen (77 K), equipped with an Agilent 5310A frequency counter. The spectrometer run under a home-made software based on Lab-View. Adequate signal to noise was obtained after 5-10 scans. In case of powdered samples, the material is inserted into 3mm quartz tubes EPR tube (Suprasil, Willmad Glass). For the Cu-MOF powdered sample, 5 mg of the material were inserted in the EPR tube. The material in the EPR tube was degassed by purging with N$_2$ for 10 minutes.

Synthesis of $N,N'$-bis(2,4-dicarboxyphenyl)-oxalamide ($H_6L$)
Oxalylchloride (1.3 g, 10 mmol) was added slowly to a stirred suspension of 2-aminoterephthalic acid (4 g, 22 mmol) in 100 mL THF. The yellow suspension was stirred for one hour and then 25 mL of NMP were added at once. The suspension turns to an almost clear yellow solution and immediately a yellow solid precipitates. The solid was collected by vacuum filtration, washed extensively with methanol (5 × 50 mL) and ether (2 × 20 mL) and dried under vacuum over silica gel for 48 h. After the treatment with methanol and ether, the solid becomes pale-white. Yield: 2.9 g (~70 %, based on the oxalylchloride). Anal. Calcd for C$_{18}$H$_{12}$N$_2$O$_{10}$: C 51.93, H 2.91, N 6.73. Found: C 51.90, H 2.88, N 6.80. $^1$H-NMR in DMSO-d$_6$ (see Fig. S15).

Synthesis of [Ca(H$_6$L)(DMA)$_2$]·2DMA (Ca-MOF)
Solid $H_6L$ (25 mg, 0.06 mmol) and solid Ca(NO$_3$)$_2$·4H$_2$O (14 mg, 0.06 mmol) were added in a 24 mL glass vial containing DMA (5 ml). The mixture was stirred for 5 min to afford a white-yellowish non-clear solution. The glass vial was sealed and heated in an isostemp oven at 100 °C for 3 days. Colorless plate-like single-crystals of Ca-MOF were formed. Yield 34mg (~70 % based on Ca). The crystals were collected by vacuum filtration and dried in a desiccator over silica gel. Anal. Calcd for C$_{34}$H$_{46}$N$_2$O$_{14}$Ca: C 50.86 , H 5.78, N 10.46; found: C 50.74, H 5.67, N 10.51. IR (KBr pellets, cm$^{-1}$): 3419 wbr, 2934 w, 2448 wbr, 1684 s, 1660 s, 1624 vs, 1575 s, 1512 vs, 1443 s, 1423 s, 1370 w, 1299 m, 1263 m, 1165 w, 1026 m, 1012 m, 949 w, 912 w, 866 w, 805 m, 769 m, 758 m, 696 w, 678 w, 596 m, 570 m, 517 m, 485 m.
Synthesis of Cu-MOF

100 mg (0.125 mmol) of Ca-MOF colorless crystals were immersed in an aqueous solution of Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O (15 ml, 0.75 mmol) and the vial was left undisturbed (no stirring or sonication) at room temperature. The solid immediately becomes pale blue. After being soaked for 24 hours, the non-crystalline blue solid was filtered, washed extensively with H\textsubscript{2}O (5 × 10 mL) and dried in a desiccator over silica gel overnight. Yield: 69 mg (97.55%, based on Ca-MOF). IR (KBr pellets, cm\textsuperscript{-1}): 3364 br, 3121 br, 1692 s, 1626 sh, 1579 s, 1514 s, 1452 s, 1421 s, 1371 s, 1295 m, 1265 m, 1225 m, 1170 m, 1078 m, 950 w, 912 w, 867 w, 802 w, 766 m, 689 w, 572 w, 517 w, 501 w. EDS analysis indicated a Cu:Ca weight % ratio of 98.19/1.81 (Cu:Ca atomic % 97.17/2.83) (see Fig. S9).

Preparation of the column

5 mg of the Ca-MOF and 0.5 g of sand (50-70 mesh SiO\textsubscript{2}) was mixed in a mortar and pestle and filled in a glass column (0.7 cm ID column). This loading was repeated nine more times, so that the column was finally filled with 50 mg of Ca-MOF and 5 g of sand. The gradual loading of the column with the Ca-MOF-sand mixture was preferred in order to achieve the best possible distribution of the Ca-MOF in the stationary phase.

Batch ion-exchange studies

A typical ion-exchange experiment of Ca-MOF with Cu\textsuperscript{2+} is the following: In a solution of Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O (3 mg, 0.0125 mmol) in water (5 mL), Ca-MOF (10 mg, 0.0125 mmol) was added as a solid. The mixture was kept undisturbed for 30 min. Then, the polycrystalline material, which had blue color, was isolated by filtration, washed several times with water and dried in a desiccator over silica gel. EDS analysis indicated a Cu:Ca weight % ratio of 75.46/24.54 (Cu:Ca atomic % 65.98/34.02) in the exchanged product. Longer soaking times (i.e. 24 h) resulted in a Cu:Ca weight % ratio of 89.71/10.29 (Cu:Ca atomic % 84.61/15.39) in the exchanged product (see Fig. S9).

The Cu\textsuperscript{2+} uptake from solutions of various concentrations was studied by the batch method at V:m ~ 1000 mL/g, room temperature and 1 h contact. These data were used for the determination of Cu\textsuperscript{2+} sorption isotherms. The variable pH ion exchange experiments and those with the drinking water samples were also carried out with the batch method at V:m ratio ~ 1000 mL/g, room temperature and 1 h contact. For the determination of the sorption kinetics, Cu\textsuperscript{2+} ion-exchange experiments of various reaction times (1-180 min) have been performed. For each experiment, a 10 mL sample of Cu\textsuperscript{2+} solution (initial Cu\textsuperscript{2+} concentration = 24.4 ppm, pH~7) was added to each vial (containing 10 mg of Ca-MOF) and the mixtures were kept under magnetic stirring for the designated reaction times. The suspensions from the various reactions were filtered and the resulting solutions were analyzed for their copper content with anodic stripping voltammetry.

Column Ion-Exchange studies

Several bed volumes of the solution were passed through the column and collected at the bottom in glass vials. The solutions were analyzed with anodic stripping voltammetry.
Batch and column ligand recycling studies

35 mg of Cu-MOF were immersed in 16 mL HCl 3M and the resulting white-greenish slurry solution was left under stirring for 12 hours. The colorless precipitate was filtered, washed extensively with H$_2$O (5×5 mL) and dried over silica gel. Yield: 22 mg (~86 %).

When 35 mg of Cu-MOF were immersed in 27 mL NaOH 0.1 M the solution immediately acquired a deep blue-green color while the colorless solid completely dissolved. After 12 hours of stirring no change was noticed and 30 mL of HCl 3 M were added under stirring. Upon the addition of HCl the previously clear blue green solution turned into a white-greenish slurry from which a gel-like precipitate formed. The slurry was then centrifuged, washed twice (2 × 10 mL) with H$_2$O, centrifuged again and the resulting colorless solid was treated with acetone to afford a white solid. The solid was isolated by filtration, washed with acetone and dried in a desiccator over silica gel for 4 days. Yield: 20 mg (~78 %).

The column (containing 50 mg of the Ca-MOF) was fully loaded with Cu$^{2+}$ and washed with 1 mM NaOH solution (30 mL). The blue-green colored effluent was treated with concentrated (~12 M) HCl acid (~5 mL). A white gel-like precipitate was immediately formed and isolated with centrifugation. The gel was washed with acetone and heated (at ~70 °C) till dryness to afford a yellowish solid. This product was treated with water (2-3 mL), isolated by filtration, washed with acetone and dried under vacuum. A white solid was thus obtained. Yield: 25 mg (96.5 %).

The purity of the recycled H$_6$L ligand was confirmed by $^1$H NMR (see Fig. S15).

References

Fig. S1. The non-regular (4.6^2;4.6.4.6) network adopted by Ca-MOF.

Fig. S2. The off-set packing of the layers of Ca-MOF. Two layers in red and blue are shown.
Fig. S3. The packing of the layers of Ca-MOF down to (0 1 1) vector (left) and down to a axis (right). Three layers are shown in ball and stick while the solvate DMA molecules occupying the pseudo rectangular channels are shown in a space filling model. Color code: Ca green, C grey, O red, N blue, H cyan.

Fig. S4. Experimental (red line) and simulated (blue line) powder X-ray diffraction patterns (pxrds) of Ca-MOF.
**Fig. S5.** TGA curve of Ca-MOF.

**Fig. S6.** Part of the structure of Ca-MOF showing potential sites (orange spheres) within the hexagonal cavities where other metal ions could occupy. Color code: Ca green, C grey, O red, N blue, H cyan.
Fig. S7. Pictures of the as synthesized Ca-MOF crystals (left) and those immersed in DMA solution containing [Cu$_2$(AcO)$_4$(H$_2$O)$_2$] for two weeks (right).

Fig. S8. Pictures of aqueous solutions (5 mL) containing Cu(NO$_3$)$_2$·3H$_2$O (left), CuCl$_2$·2H$_2$O (middle) and [Cu$_2$(AcO)$_4$(H$_2$O)$_2$] (right), respectively, few seconds (5-10) after the addition of 10 mg Ca-MOF (top) and 1-2 minutes after the addition (bottom). The Ca$^{2+}$/Cu$^{2+}$ in all three vials is 1:1.
Fig. S9. EDS spectra of Cu$^{2+}$ exchanged Ca-MOF. Top: 1:1 Cu$^{2+}$/Ca$^{2+}$ soaking time 30 min. Middle: 1:1 Cu$^{2+}$/Ca$^{2+}$ soaking time 24 h. Bottom: 6:1 Cu$^{2+}$/Ca$^{2+}$ soaking time 48 h.
Fig. S10. The $^1$H-NMR spectra of Ca-MOF soaked for 2 days in D$_2$O (bottom) and in a D$_2$O solution of Zn(NO$_3$)$_2$-4H$_2$O with a 1:1 Zn$^{2+}$/Ca$^{2+}$ ratio.

Fig. S11. The IR spectra (KBr discs) of the as synthesized Ca-MOF (bottom, black line), of Ca-MOF soaked in H$_2$O for 3 days (middle, blue line) and of Cu-MOF (top, red line).
Fig. S12. TGA curve of [Ca(H₄L)(H₂O)₂]·3H₂O obtained by immersing Ca-MOF in H₂O for 3 days, followed by filtration and drying over silica gel in a desiccator for 3 days.

Fig. S13. Experimental powder X-ray diffraction pattern of Cu-MOF.
Fig. S14. TGA curve of Cu-MOF.

Fig. S15. The \(^1\)H-NMR spectra in DMSO-d\(_6\) of the as synthesized H\(_6\)L (bottom, red line), of H\(_6\)L recycled by treating the Cu-MOF with HCl (middle, green line) and of H\(_6\)L recycled by treating the Cu-MOF with NaOH, followed by HCl (top, blue line).