**Supplementary information**

A picture containing photo, different, bunch, filled

Description automatically generated

**Fig. S1.** FESEM micrographs of the cross section of all PVSi membrane samples.



**Fig. S2.** Raman mapping of siloxene distribution on the surface of all PVSi membrane samples

A picture containing nature, cake, lit, sitting

Description automatically generated

**Fig. S3.** AFM micrographs of the surface of all PVSi membrane samples.



**Fig. S4.** FTIR spectra of all PVSi membrane samples.

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**Fig. S5.** UV-Vis calibration curves for dyes: (a) Rose Bengal (RB); (b) Reactive Black 5 (RB5); (c) Brilliant Blue G (BB); (d) Direct Red 23 (DR23); (e) Congo Red (CR); (f) Acid Red 1 (AR1) and (g) Methyl Orange (MO).

A screenshot of a cell phone

Description automatically generated

**Fig. S6.** The correlation between the CAA and hydrated radius of several dyes with known hydrated radii obtained from Table S3. This correlation was used to estimate hydrated radius of the dyes [1, 2]

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**Fig. S7.** Schematics for the structures of (A) CaSi2 and (B) deintercalation of Ca from CaSi2

Chart, line chart

Description automatically generated

**Fig. S8.** UV-Vis spectra of the feed (purple), permeate (blue) and retentate (red) of Congo red dye rejection for PVSi-075 membrane sample.

Table S1. XRD pattern analysis of PVSi membranes.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample  Name | (020) | | | | | (110) | | | | | (021) | | | | |
| **2*θ***  **(°)** | ***d*-spacing**  **(Å)** | **Wa)**  **(°)** | **Hb)**  **(CPS)** | **HW/Hc)** | **2*θ***  **(°)** | ***d*-spacing**  **(Å)** | **W**  **(°)** | **H**  **(CPS)** | **HW/H** | **2*θ***  **(°)** | ***d*-spacing**  **(Å)** | **W**  **(°)** | **H**  **(CPS)** | **HW/H** |
| PVSi-0 | 18.31 | 4.84 | 1.851 | 120 | 0.008 | 19.94 | 4.44 | 1.489 | 181 | 0.004 | 26.54 | 3.38 | 2.571 | 101 | 0.012 |
| PVSi-025 | 18.31 | 4.84 | 1.853 | 127 | 0.007 | 19.94 | 4.44 | 1.485 | 185 | 0.004 | 26.65 | 3.34 | 2.151 | 103 | 0.010 |
| PVSi-050 | 18.32 | 4.84 | 1.833 | 151 | 0.006 | 19.94 | 4.44 | 1.487 | 201 | 0.004 | 26.72 | 3.33 | 2.155 | 121 | 0.009 |
| PVSi-075 | 18.32 | 4.83 | 1.751 | 169 | 0.005 | 19.95 | 4.43 | 1.483 | 299 | 0.002 | 26.97 | 3.30 | 2.511 | 167 | 0.007 |
| PVSi-100 | 18.32 | 4.83 | 1.853 | 181 | 0.005 | 19.95 | 4.43 | 1.485 | 213 | 0.003 | 26.78 | 3.32 | 2.171 | 160 | 0.007 |
| PVSi-150 | 18.32 | 4.83 | 1.851 | 183 | 0.005 | 19.95 | 4.43 | 1.483 | 241 | 0.003 | 26.81 | 3.32 | 2.593 | 189 | 0.007 |

a): peak width; b): peak height, unit of counts per second; c): ratio of half-width to height

Table S2. Summary of separation performance of PVSi-075 in water including molecular weights, rejections and mass balances for various dyes and salts.

|  |  |  |  |
| --- | --- | --- | --- |
| Dyes / Salts | Molecular Weight (Da) | Rejection (%) | Mass Balance (%) |
| RB | 1017.64 | 94 ± 3 | 99 ± 1 |
| RB5 | 991.82 | 94 ± 1 | 99 ± 1 |
| BB | 854.02 | 94 ± 2 | 99 ± 1 |
| DR23 | 813.72 | 95 ± 2 | 95 ± 1 |
| CR | 696.66 | 98 ± 2 | 99 ± 1 |
| AR1 | 509.42 | 87 ± 2 | 99 ± 1 |
| MO | 327.33 | 68 ± 1 | 99 ± 1 |
| Na2SO4 | 142.04 | 44 ± 1 | 96 ± 1 |
| MgSO4 | 120.37 | 39 ± 1 | 95 ± 1 |
| MgCl2 | 95.21 | 28 ± 1 | 96 ± 1 |
| NaCl | 58.44 | 15 ± 1 | 96 ± 1 |

Table S3. 3D chemical structures with CAA and hydrated radii of several dyes from the literature [1, 2].

|  |  |  |  |
| --- | --- | --- | --- |
| Dyes | 3D Chemical Structurea) | CAA (Å2) | Hydrated Radii (Å) |
| Methyl Red | A necklace on a wooden surface  Description automatically generated | 501.11 | 4.87 |
| Methyl Orange | A necklace on a wooden table  Description automatically generated | 515.87 | 4.96 |
| Methylene Blue | A necklace on a wooden surface  Description automatically generated | 530.26 | 5.04 |
| Orange G | A necklace on a wooden table  Description automatically generated | 563.01 | 5.21 |
| Rose Bengal | A picture containing indoor, wooden, table, small  Description automatically generated | 697.21 | 5.88 |
| Rhodamine B | A picture containing accessory, table, necklace, display  Description automatically generated | 757.02 | 6.15 |
| Methyl Blue | A picture containing indoor, air, display, flying  Description automatically generated | 1026.64 | 7.29 |
| Brilliant Blue G | A close up of a necklace  Description automatically generated | 1211.60 | 7.98 |

a): Colours for atoms: dark grey (carbon), white (hydrogen), blue (nitrogen), red (oxygen), yellow (sulphur), green (chlorine) and pink (iodine).

Table S4. 3D chemical structures and the hydrated radii of the dyes estimated from CAA

|  |  |  |  |
| --- | --- | --- | --- |
| Dyes | 3D Chemical Structurea) | CAA (Å2) | Hydrated Radii (Å) |
| RB | A picture containing indoor, wooden, table, small  Description automatically generated | 712.84 | 5.87 |
| RB5 | A picture containing table, display, sitting, small  Description automatically generated | 1250.91 | 8.23 |
| BB | A close up of a necklace  Description automatically generated | 1198.92 | 8.00 |
| DR23 | A picture containing accessory, table, brace, necklace  Description automatically generated | 1057.01 | 7.38 |
| CR | A picture containing table, display, necklace, sitting  Description automatically generated | 970.77 | 7.00 |
| AR1 | A necklace on a table  Description automatically generated | 635.74 | 5.53 |
| MO | A necklace on a wooden table  Description automatically generated | 536.54 | 5.03 |

a): Colours for atoms: dark grey (carbon), white (hydrogen), blue (nitrogen), red (oxygen), yellow (sulphur), green (chlorine) and pink (iodine).

Table S5. Summary of dyes and salts used in this work

|  |  |  |  |
| --- | --- | --- | --- |
| Dyes / Salts | Molecular Weight  (Da) | Dye Content  / Salt Purity | Supplier |
| Rose Bengal (RB) | 1017.64 | 95% | *Sigma Aldrich* |
| Reactive Black 5 (RB5) | 991.82 | ≥ 50% |
| Brilliant Blue G (BB) | 854.02 | ~ 30% |
| Direct Red 23 (DR23) | 813.72 | 30% |
| Congo Red (CR) | 696.66 | ≥ 35% |
| Hexaphenylbenzene (HPB) | 534.69 | 98% |
| Acid Red 1 (AR1) | 509.42 | 60% |
| Sudan IV (SB) | 380.44 | ≥ 80% |
| Methyl Orange (MO) | 327.33 | 85% |
| Sodium Sulphate (Na2SO4) | 142.04 | > 99% |
| Magnesium Sulphate (MgSO4) | 120.37 | > 99.5% |
| Magnesium Chloride (MgCl2) | 95.21 | > 98% | *Acros Organics* |
| Sodium Chloride (NaCl) | 58.44 | ≥ 99% | *Sigma Aldrich* |

**References**

[1] A. Akbari, P. Sheath, S.T. Martin, D.B. Shinde, M. Shaibani, P.C. Banerjee, R. Tkacz, D. Bhattacharyya, M. Majumder, Large-area graphene-based nanofiltration membranes by shear alignment of discotic nematic liquid crystals of graphene oxide, Nat Commun, 7 (2016).

[2] P. Liu, C. Milletto, S. Monti, C.T. Zhu, A.P. Mathew, Design of ultrathin hybrid membranes with improved retention efficiency of molecular dyes, Rsc Adv, 9 (2019) 28657-28669.