

Electronic Supplementary Information (ESI)

Highly transparent, amphiphobic, stable and multi-purpose poly(vinyl chloride) metallopolymer for anti-fouling and anti-stain coatings

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Supplementary text

UV-visible spectra

The UV-visible absorbance was monitored by a UV-visible spectrophotometer in the range of 200-450 nm. The reference THF solution showed a straight line with no absorbance peak (Fig. S2A (a)). PVC
15 in the THF solution showed a sharp peak at 216 nm as well as some weak peaks at 203, 206, 208, 232, 236, 253 and 260 nm (Fig. S2A (b)).¹ Fe (III) in water showed a broad spectrum at 212-250 nm and 310-370 nm (Fig. S2A (c)). The phase separated Fe (III) in toluene from toluene-water mixture showed a shift in the broad peak at 212-278 nm. Two new broad bands were obtained at 290-340 nm and 345-410 nm (Fig. S2A (d)). The TMSH monomer showed a strong sharp peak at 235 nm (Fig.
20 S2A (e)). The FeSH precursor (by a reaction of TMSH monomer and Fe (III) in a toluene solution) showed a broad band at 215-275 nm, and decrease in the broad shift at 290-340 nm, and 345-410 nm (Fig. S2A (f) and Fig. S2B (a)). The decrease in broad peak intensity was attributed to the reduction of Fe (III) to Fe (II) ions by the mercapto functional group. Two broad bands for the FeSH precursor disappeared in the PVCFeS metallopolymer and a new band appeared at 336 nm by continuing the
25 reaction time (Fig. S2A (g-j) and Fig. S2B (b)).² This might be due to the complete reaction of

mercapto functional groups in the TMSH monomer by grafting with PVC. The sharp peaks at 220, 257, 263, and 270 nm were shifted, and weak peaks were observed at 204 and 208 nm, by continuing the reaction time to 24 h. The intensity of the sharp peaks at 220 nm increased slightly with increasing the reaction time and shifted slightly to 224 nm. The other intensity peaks appeared at 253, 257, 263, 270, and 336 nm were also increased slightly with increasing reaction time. PVCFeS-SiSH (SiSH-0.05 phr) metallopolymer also showed a sharp peak at 235 nm and a reduced intensity at 336 nm (Fig. S2A (k) and Fig. S2B (c)). The PVCFeS-SiMe (SiMe-0.01 phr) metallopolymer showed the peaks at 253, 263 and 270 nm and a complete decrease in the band at 336 nm (Fig. S2A (l) and Fig. S2B (d)). This suggests that the new band at 336 nm might be due to the presence of thio groups in the metallopolymer, which indicates the complete grafting of FeSH to the PVC backbone. On the other hand, the introduction of mercapto functional groups may decrease the intensity of the band at 336 nm.

¹H-NMR Spectroscopy

The ¹H-NMR spectra of PVC, Fe (III) in toluene, FeSH, PVCFeS, PVCFeS-SHSi (SiSH-0.05 phr), and PVCFeS-SiMe (SiMe-0.01 phr) were analyzed in CDCl₃, whereas the ¹H-NMR spectra of TMSH was analyzed in DMSO (Fig. S4 (a-g)).

For PVC; $\delta = 1.16$ ppm (dd, $J = 4.4$ Hz, 6.0 Hz), $\delta = 1.19$ ppm (s), $\delta = 1.21$ ppm (t, $J = 7.0$ Hz), $\delta = 1.51$ ppm (s), $\delta = 2.06$ (m), $\delta = 2.29$ ppm (m), $\delta = 3.70$ ppm (m), $\delta = 3.47$ ppm (s), $\delta = 3.45$ ppm (s), $\delta = 4.43$ ppm (d, $J = 6.7$ Hz), $\delta = 4.56$ ppm (s).³

For TMSH monomer; $\delta = 0.94$ ppm (t, H_d, $J = 7.4$ Hz), $\delta = 1.52$ ppm (s, H_a), $\delta = 2.50$ ppm (dd, H_e, $J = 5.2$ Hz, $J = 9.9$ Hz), $\delta = 2.50$ ppm DMSO, $\delta = 2.75$ ppm (t, H_c, $J = 9.5$ Hz), $\delta = 2.50$ ppm (t, H_b, $J = 6.8$ Hz), $\delta = 4.11$ ppm (s, H_f).

For FeSH precursor; $\delta = 0.88$ ppm (t, $J = 6.7$ Hz), $\delta = 1.27$ ppm (s), $\delta = 1.47$ ppm (s), $\delta = 1.49$ ppm (s), $\delta = 1.64$ ppm (d, $J = 24.3$ Hz), $\delta = 2.14$ ppm (s), $\delta = 2.64$ ppm (t, $J = 6.6$ Hz), $\delta = 2.74$ ppm (t, $J = 6.5$ Hz), $\delta = 2.88$ ppm (t, $J = 6.1$ Hz), $\delta = 4.04$ ppm (s).

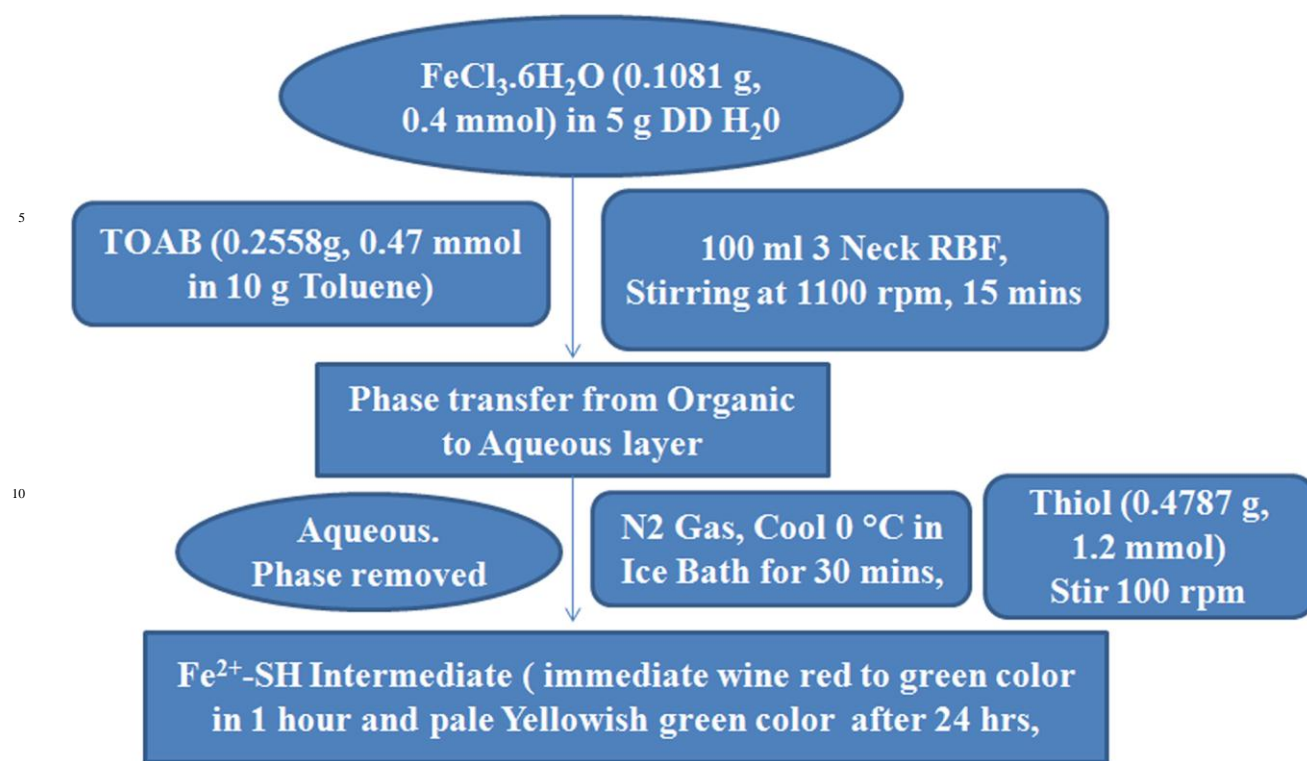
For PVCFeS metallopolymer; $\delta = 0.85$ ppm (m), $\delta = 1.25$ ppm (s), $\delta = 1.55$ ppm (s), $\delta = 1.85$ ppm (m), $\delta = 2.17$ ppm (s), $\delta = 2.35$ ppm (s), $\delta = 2.76$ ppm (s), $\delta = 2.92$ ppm (s), $\delta = 3.47$ ppm (d, $J = 5.9$ Hz), $\delta = 3.74$ ppm (t, $J = 7.6$ Hz), $\delta = 4.07$ ppm (s), $\delta = 4.47$ ppm (s), $\delta = 4.58$ ppm (s).

For PVCFeS-SiSH (SiSH-0.05 phr) metallopolymer; $\delta = 0.05$ ppm (s), $\delta = 0.13$ ppm (s), $\delta = 0.74$ ppm (s), $\delta = 1.19$ ppm (m), $\delta = 1.24$ ppm (s), $\delta = 1.37$ ppm (s), $\delta = 1.52$ ppm (s), $\delta = 1.69$ ppm (s), $\delta = 2.15$ ppm (s), $\delta = 2.54$ ppm (d, $J = 5.4$ Hz), $\delta = 2.68$ ppm (s), $\delta = 3.32$ ppm (s), $\delta = 3.46$ ppm (d, $J = 7.7$ Hz), $\delta = 3.52$ ppm (m), $\delta = 4.06$ ppm (s).

For PVCFeS-SiMe (SiMe-0.01 phr) metallopolymer; $\delta = -0.02$ ppm (s), $\delta = 0.13$ ppm (s), $\delta = 0.86$ ppm (s), $\delta = 1.20$ ppm (dd, $J = 8.5$ Hz, $J = 17.1$ Hz), $\delta = 1.52$ ppm (s), $\delta = 1.83$ ppm (s), $\delta = 2.06$ ppm (s), $\delta = 2.15$ ppm (s), $\delta = 2.33$ ppm (s), $\delta = 3.46$ ppm (d, $J = 6.6$ Hz), $\delta = 4.43$ ppm (s), $\delta = 4.56$ ppm (s), $\delta = 4.67$ ppm (s).

High resolution transmission electron microscopy (HR-TEM)

The porous (membrane) morphology of the PVCFeS metallopolymer (Fig. S6 and S7a and b in ESI) was also appeared by the addition of 0.01 phr MPTMS. The surface morphology also showed very less adhesion of functionalised SiSH groups on the surface. On the other hand, the surface morphology was changed partially by the adhesion of SiSH groups on the PVCFeS metallopolymer surface with increasing the ratios of MPTMS to 0.05 phr, 0.1 phr and 0.2 phr (Fig. S7 (c-h)). Meanwhile, the thickness of the PVCFeS metallopolymer was increased partially on increasing the amount of MPTMS. The results highlight the reason for the reduced transparency of the PVCFeS metallopolymer obtained with 0.01 phr of MPTMS in comparison with that of higher amount of MPTMS. The ratio of MPTMS to PVCFeS metallopolymer also plays a major role in enhancing the transparency of the coated glass substrate.



Scheme S1. Preparation of the trimethylolpropane tris(ferro-mercaptopropionate) (FeSH) precursor.



Fig. S1 Stability of the PVCFeS-SiSH metallopolymer solutions of various ratios (0.01, 0.05, 0.1 and 0.2 phr) of SiSH, which have been stored at room temperature for 6 weeks.

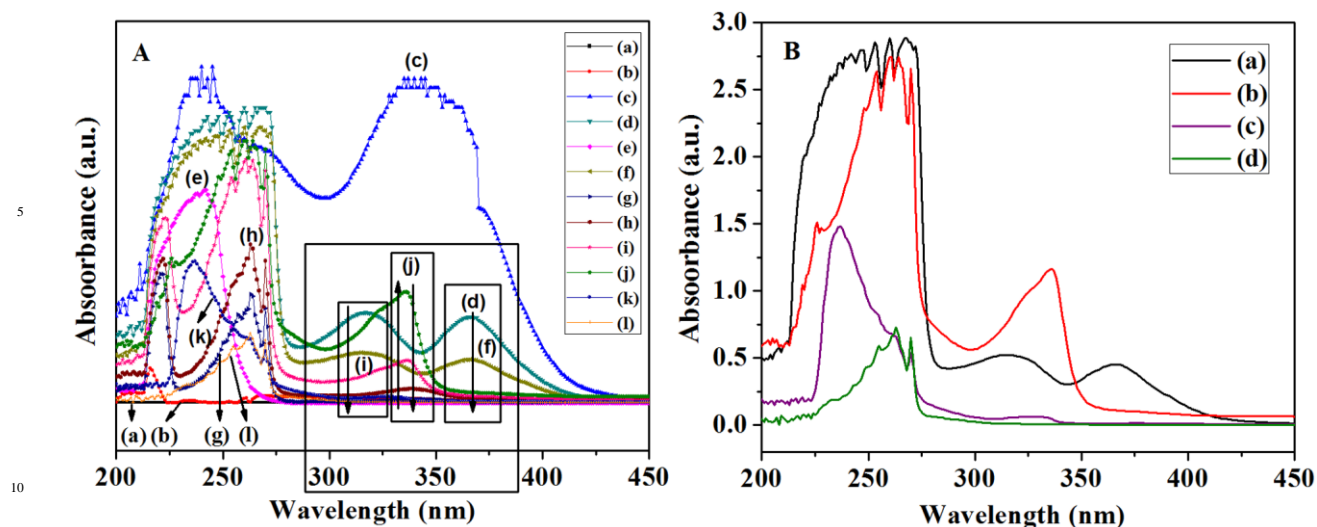


Fig. S2 (A) UV-visible spectra of (a) reference (THF), (b) PVC in THF, (c) Fe (III) in water, (d) Fe (III) in toluene, (e) TMSH, (f) FeSH, (g) PVCFeS in 30 mins, (h-j) PVCFeS stirred for 6, 12 and 24 h, (k and l) PVCFeS-SiSH (SiSH-0.05 phr) and PVCFeS-SiMe (SiMe-0.01 phr) metallopolymer solutions after 24 h. B) UV-visible spectra of (a-d) FeSH, PVCFeS, PVCFeS-SiSH (SiSH-0.05 phr) and PVCFeS-SiMe (SiMe-0.01 phr) metallopolymer solutions.

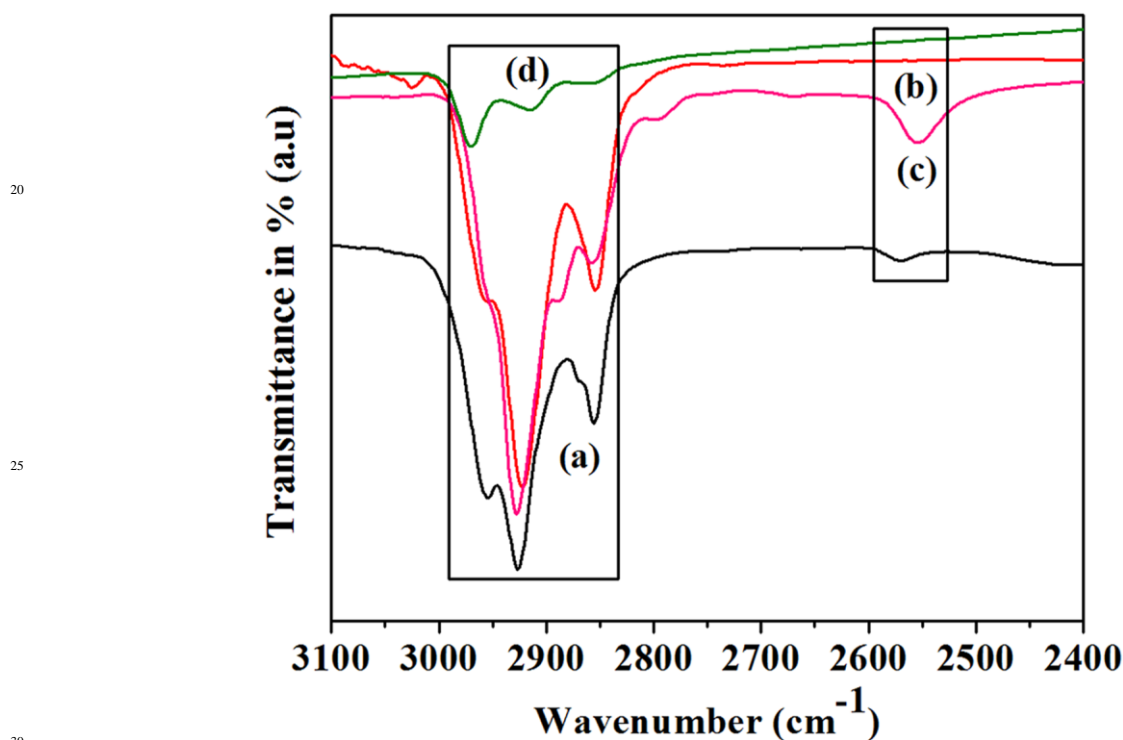


Fig. S3 FTIR spectra (liquid samples) in the range of 2400-3100 cm⁻¹ of (a) FeSH, (b) PVCFeS after 24 h, (c) PVCFeS-SiSH (SiSH-0.05 phr) and (d) PVCFeS-SiMe (SiMe-0.01 phr) metallopolymer solutions after 24 h.

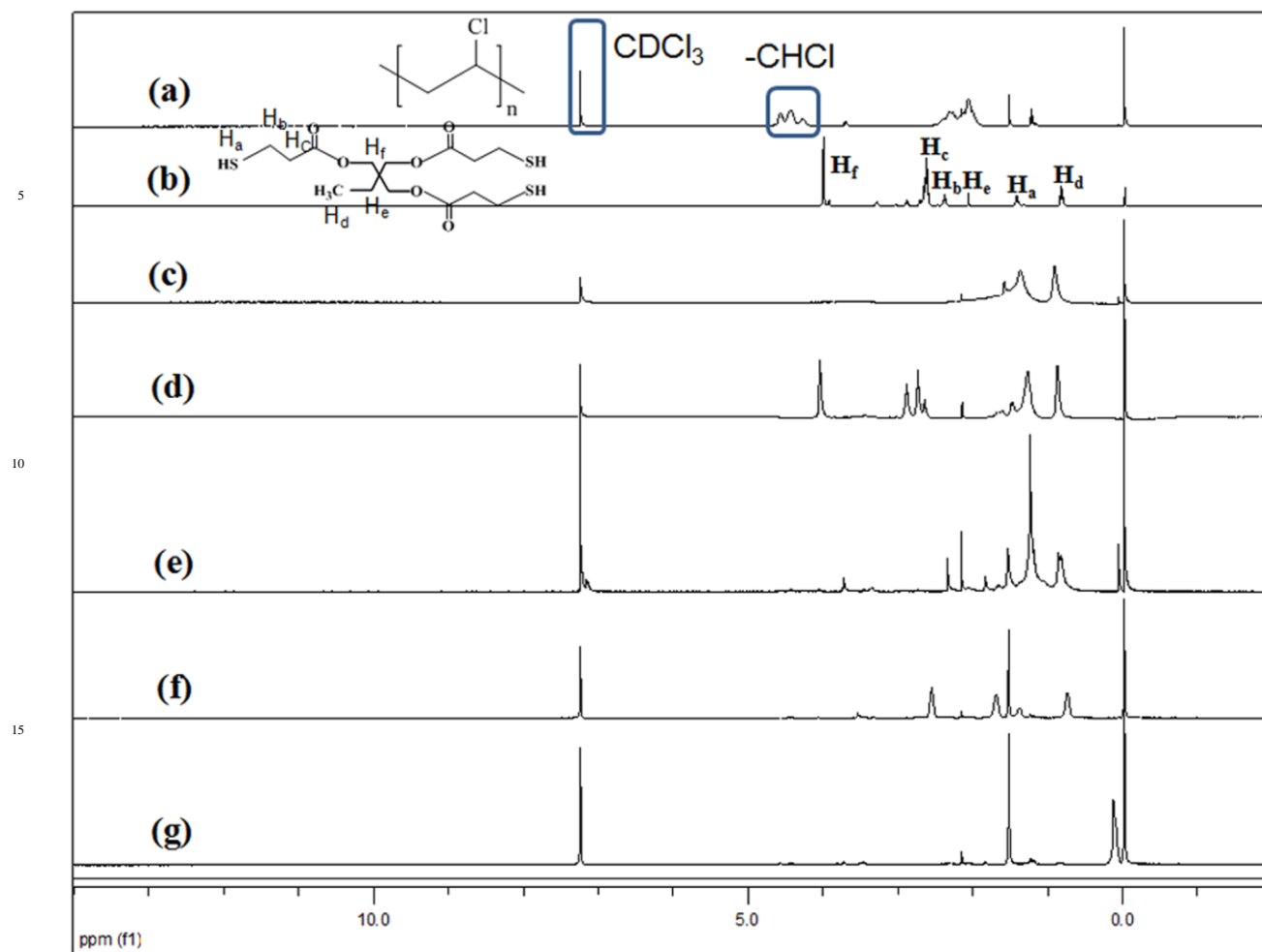
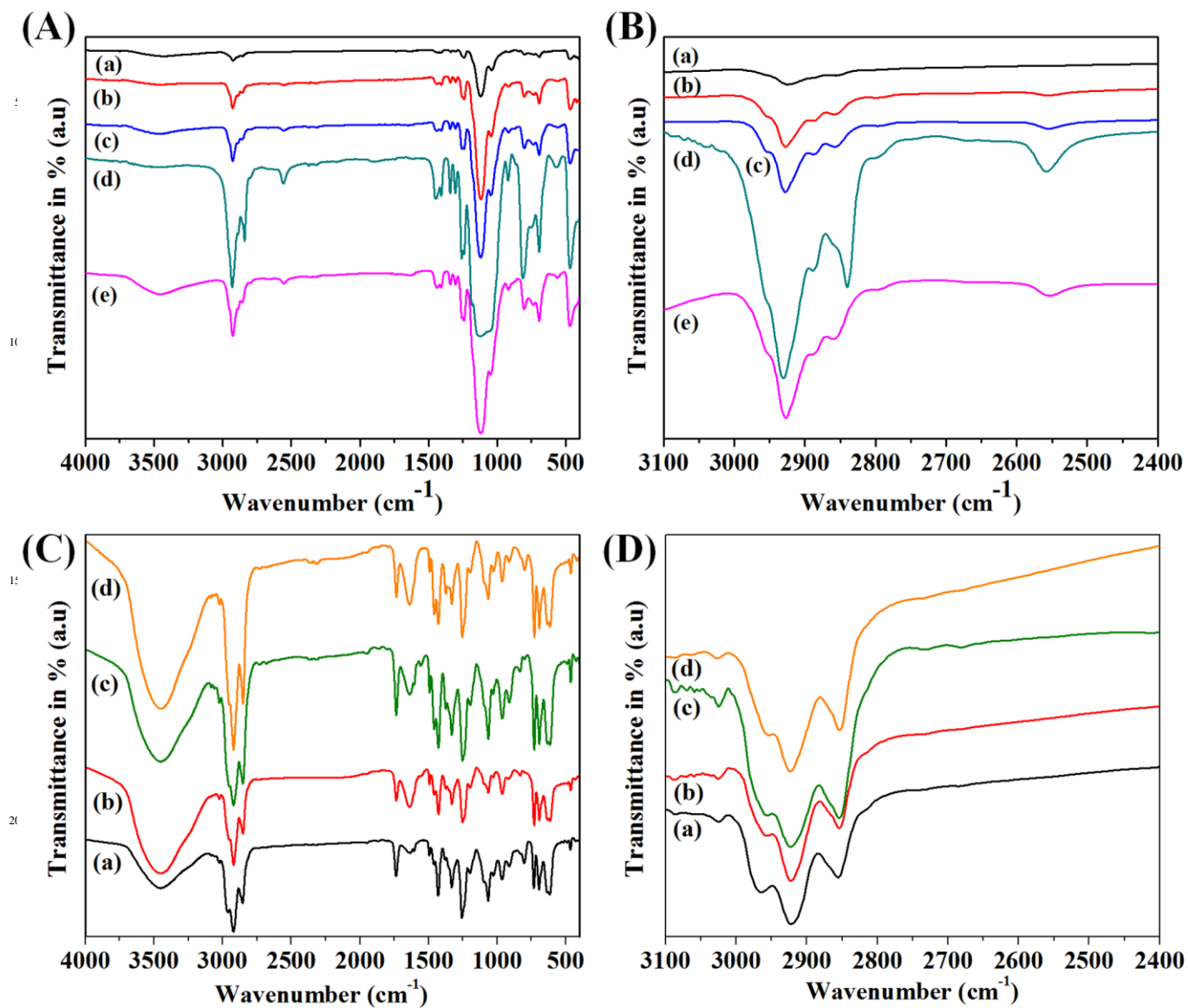


Fig. S4 ¹H-NMR spectra of (a) PVC in CDCl₃, (b) TMSH in DMSO, (c) Fe (III) phase separated by toluene, (d) FeSH, (e) PVCFeS, (f) PVCFeS-SiSH (SiSH-0.05 phr) and (g) PVCFeS-SiMe (SiMe-0.01 phr) in CDCl₃.



25 **Fig. S5** (A and B) PVCFeS-SiSH metallopolymer solutions at various ratios of SiSH ((a) 0.01, (b) 0.05, (c) 0.1 and (d) 0.2 phr), when stored at room temperature for 6 weeks. (e) PVCFeS-SiSH (SiSH-0.05 phr) metallopolymer solution stored at room temperature for 1 year. (C and D) FTIR spectra (liquid samples) of PVCFeS metallopolymer solutions with various ratios of metal ions ((a) 0.1081 g, (b) 0.2162 g, (c) 0.3243 g and (d) 0.4324 g).

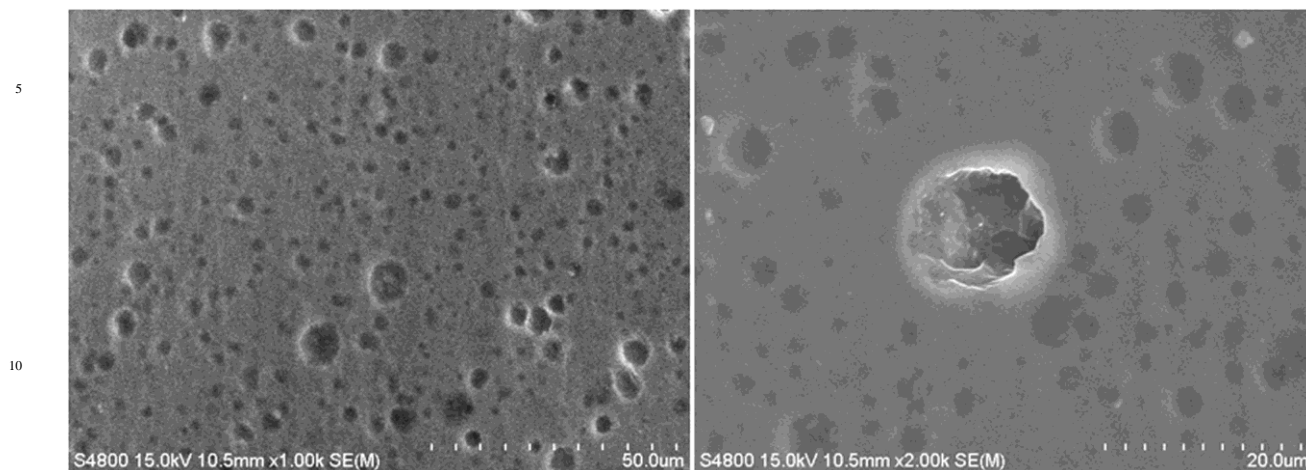


Fig. S6 HR-SEM images of the PVCFeS metallopolymer film (membrane) prepared at 40 °C in 24 h by a casting method.

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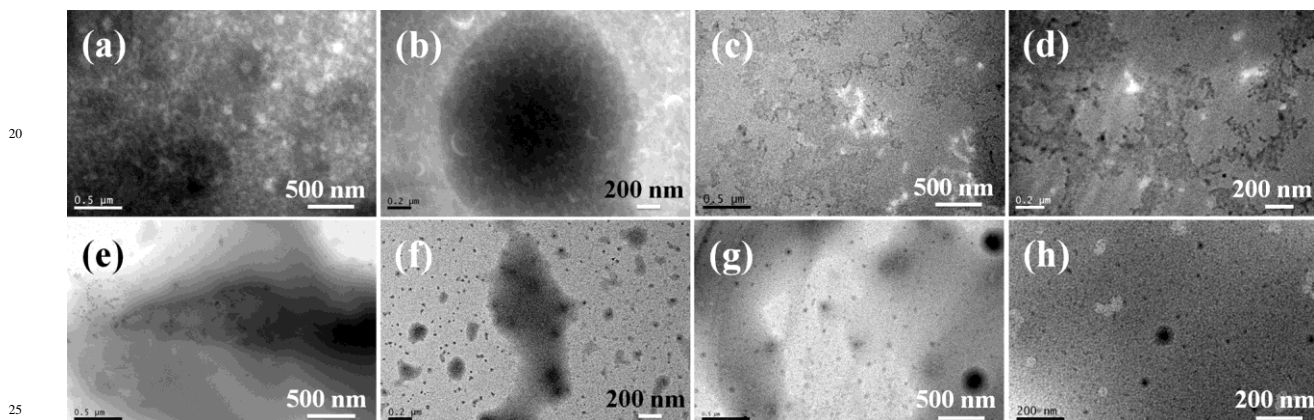


Fig. S7 HRTEM images of PVCFeS-SiSH metallopolymers prepared with various amounts of SiSH groups ((a, b) 0.01 phr, (c, d) 0.05 phr, (e, f) 0.1 phr, and (g, h) 0.2 phr) at two different magnification; (a,c,e, and g) with lower magnification, while (b,d,f, and h) with higher magnification) .

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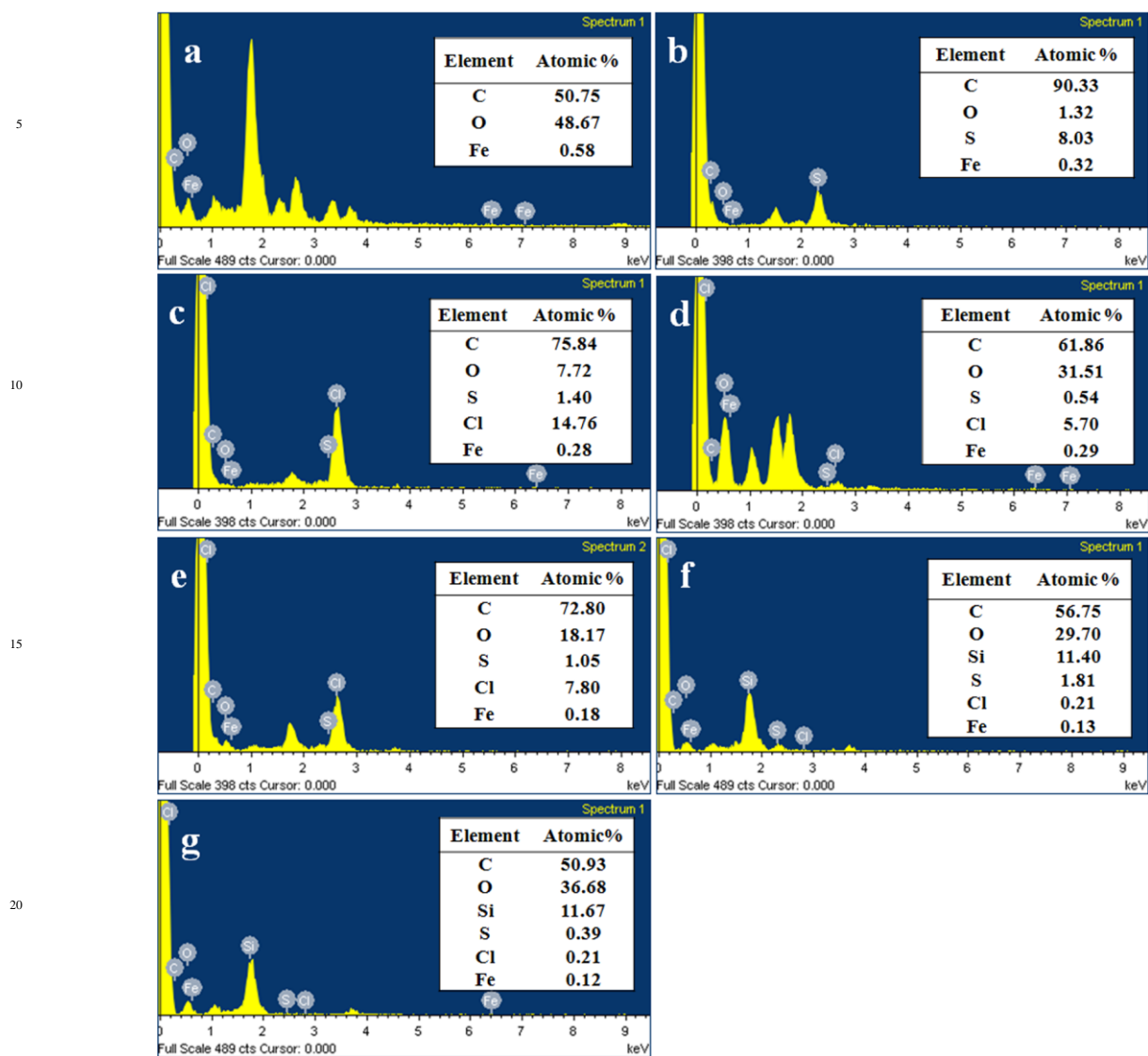


Fig. S8 HR-SEM-ED spectra of spin coated samples of (a) Fe (III) in toluene at RT, (b-e) FeSH, PVCFeS at RT, 40 °C and 80 °C for 24 h. (f and g) PVCFeS-SiSH (SiSH-0.05 phr) and PVCFeS-SiMe (SiMe-0.01 phr) metallopolymers cured at 150 °C for 24 h.

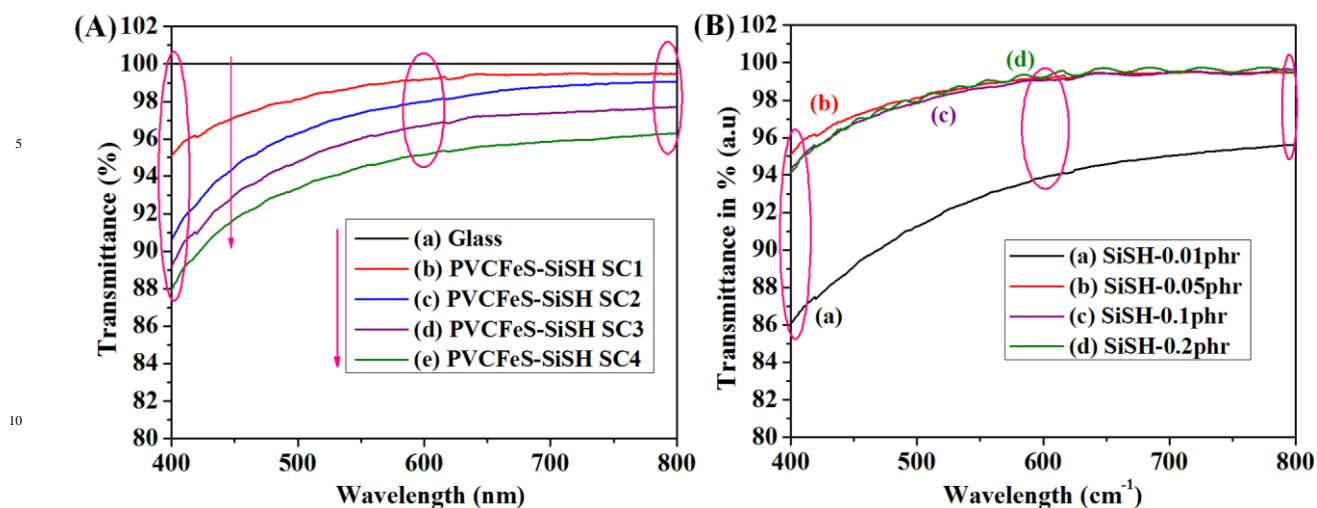
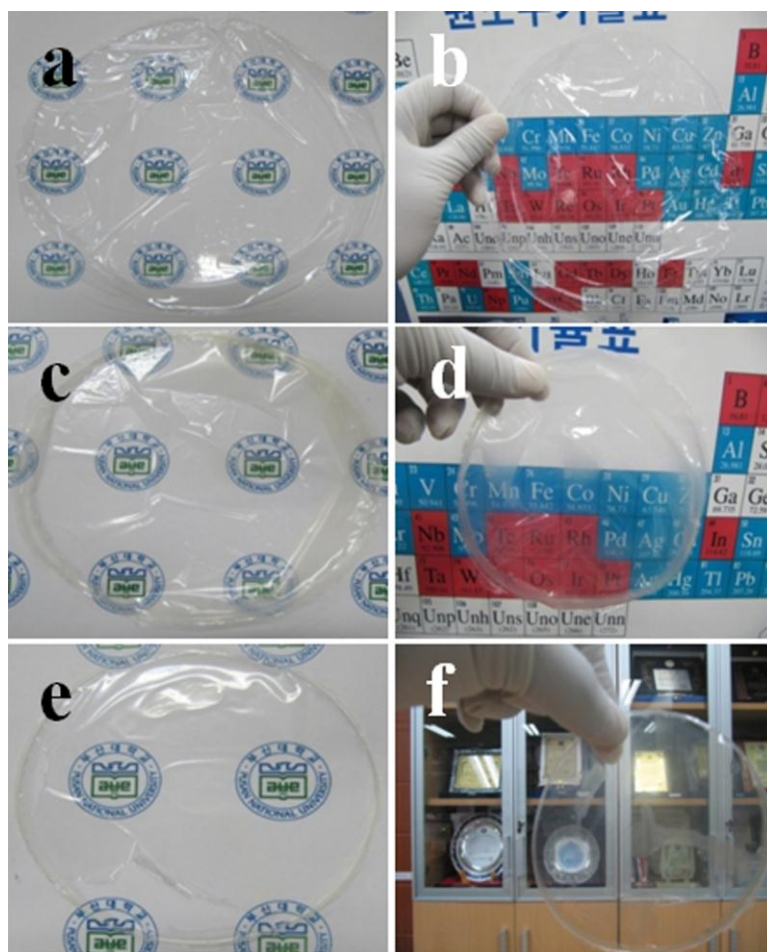


Fig. S9 (A) UV-visible transmittance spectra of (a) glass substrate (reference), (b-e) PVCFeS-SiSH (0.05 phr SiSH) metallopolymers spin coated for 1 to 4 (SC1, SC2, SC3 and SC4) times on the same substrate at 1000 rpm for 60 S. (B) PVCFeS-SiSH metallopolymers prepared with various amounts of SiSH groups ((a-d) 0.01 phr, 0.05 phr, 0.1 phr and 0.2 phr).



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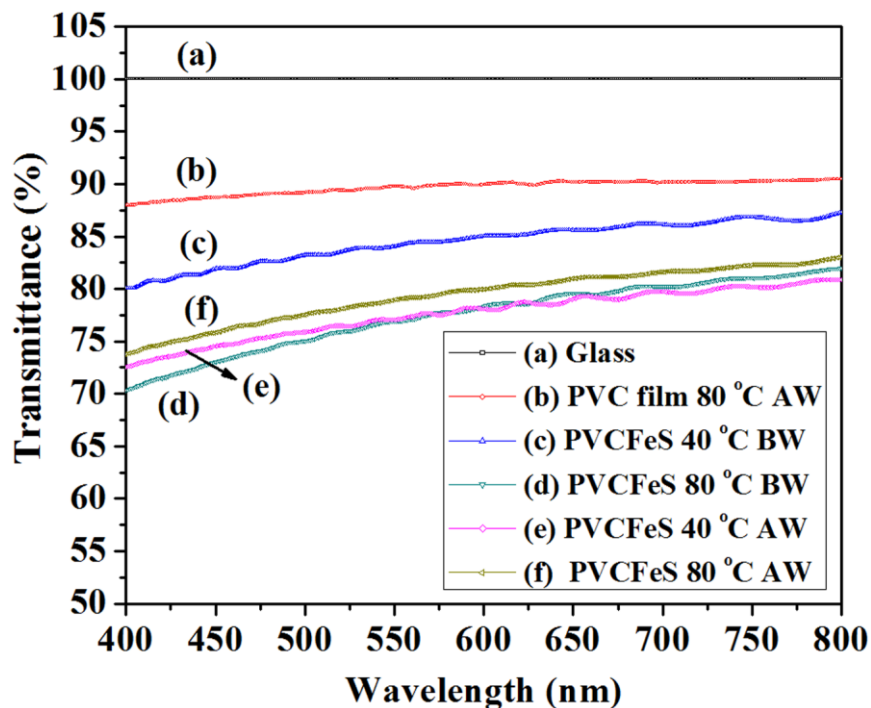
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20 **Fig. S10** Optical images of highly transparent films obtained from a PVC solution casted at (a and b)
80 °C and cured for 5 h, and PVCFeS metallopolymer films at (c and d) 40 °C and (e and f) 80 °C for
24 h.

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15 **Fig. S11** UV-visible transmittance spectra of (a) glass substrate (reference), (b) PVC film prepared at 80 °C for 5 h, washed with water and dried overnight at 80 °C. PVCFeS metallopolymer films prepared by casting and cured at (c) 40 °C, (d) and 80 °C (before washing-BW) for 24 h. The films washed in water and cured overnight at the respective temperatures ((e) 40 °C, and (f) 80 °C, after
20 washed-AW).

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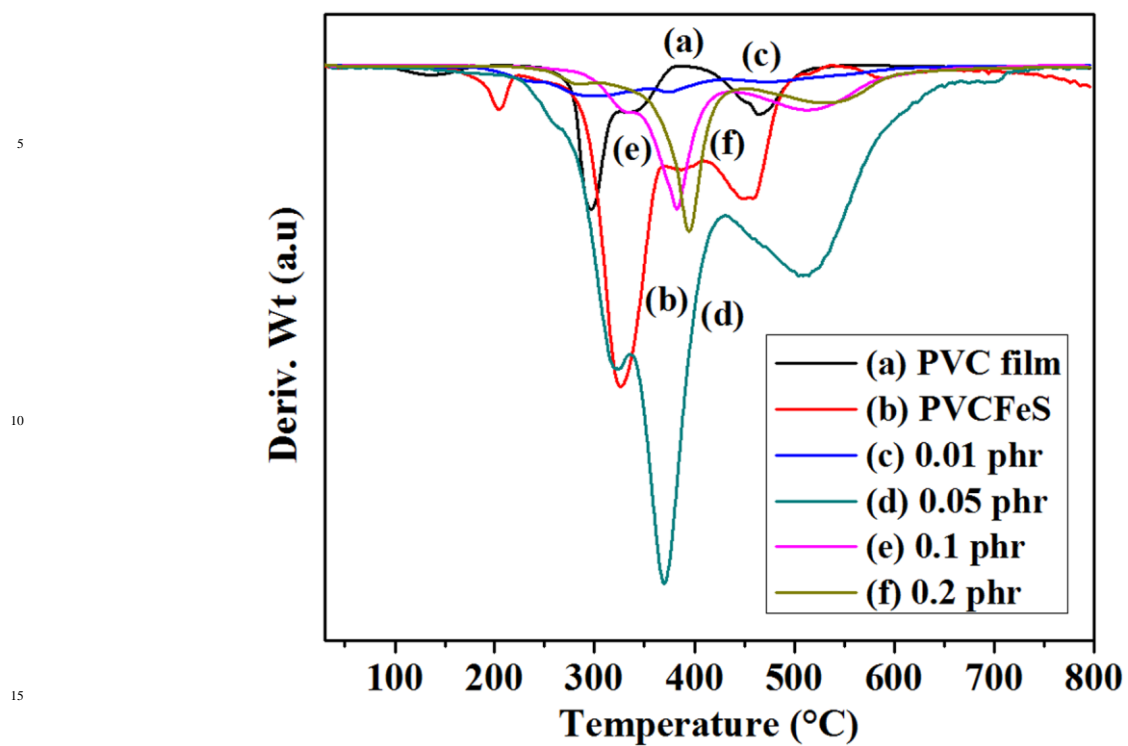
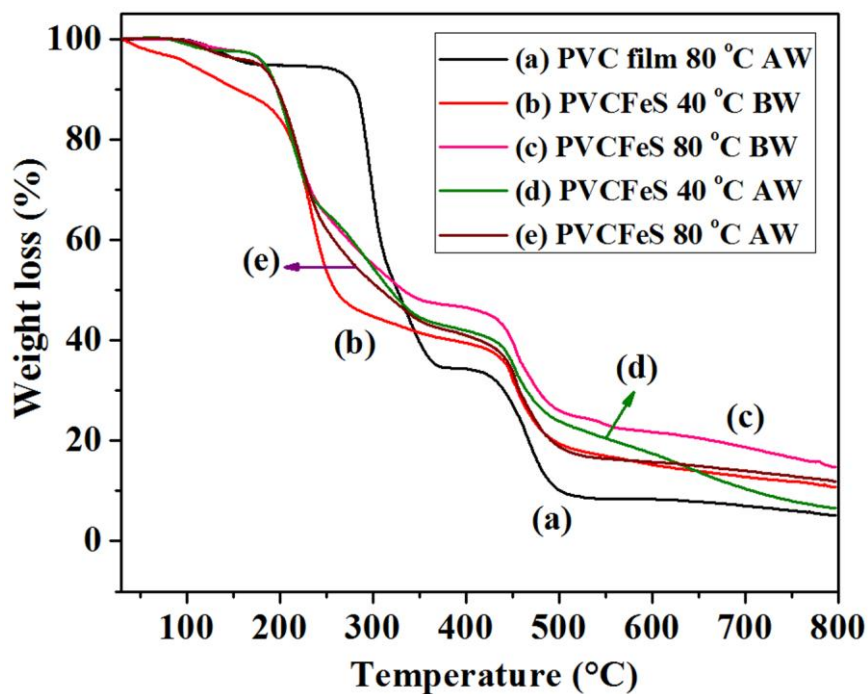


Fig. S12 TGA derivative curves of PVC film, PVCFeS, and PVCFeS-SiSH metallopolymers of various ratios (0.01, 0.05, 0.1 and 0.2 phr) of SiSH.



20 **Fig. S13** TGA of (a) PVC film prepared at 80 °C for 5 h, washed with water and dried overnight at 80 °C. PVCFeS metallopolymer films prepared by casting and cured at (b) 40 °C, (c) and 80 °C (before washing-BW) for 24 h. The films washed in water and cured overnight at the respective temperatures ((d) 40 °C and (e) 80 °C, after washed-AW).

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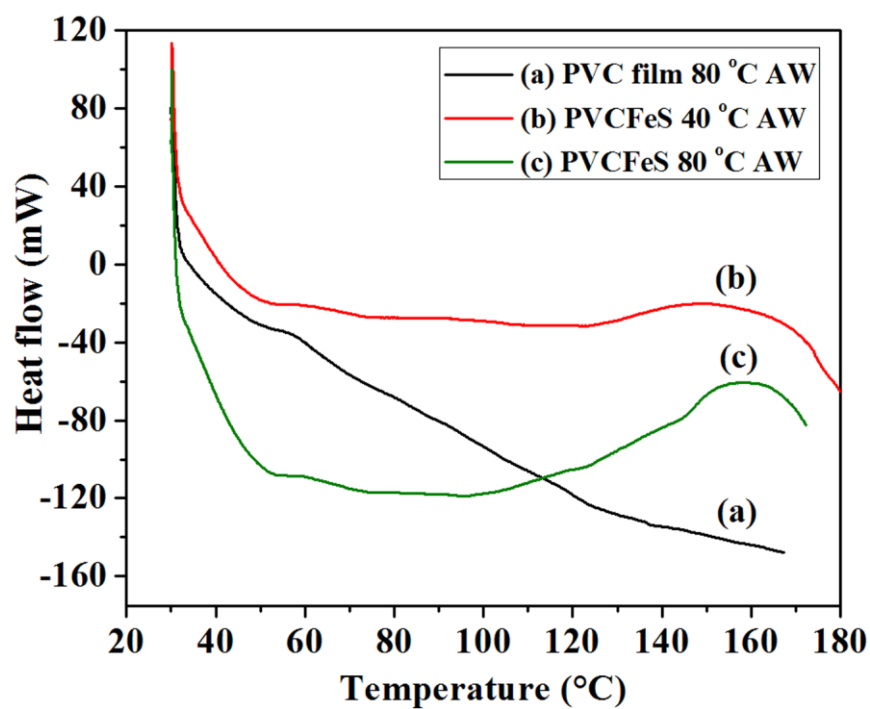


Fig. S14 DSC curve of (a) PVC film prepared at 80 °C in 5 h, washed with water and dried overnight at 80 °C. PVCFeS metallopolymer films prepared by casting and cured at (b) 40 °C, (c) and 80 °C, followed by washing in water and curing overnight at the respective temperatures (after washed-AW).

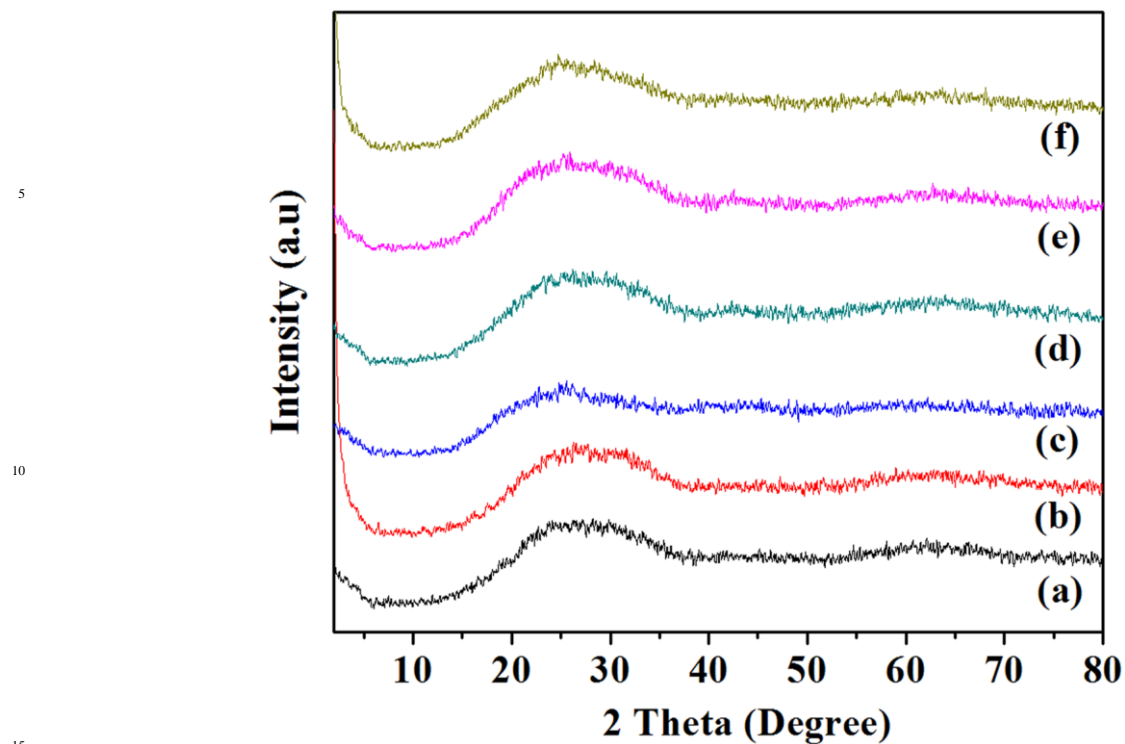


Fig. S15 XRD patterns of (a) PVC powder, (b) PVC film prepared at 80 °C for 5 h, washed with water and dried overnight at 80 °C. PVCFeS metallopolymer films prepared by casting and curing at (c) 40 °C, (d) and 80 °C (before washing-BW) for 24 h. The films were washed in water and cured overnight at the respective temperatures ((e) 40 °C, and (f) 80 °C, after washed-AW).

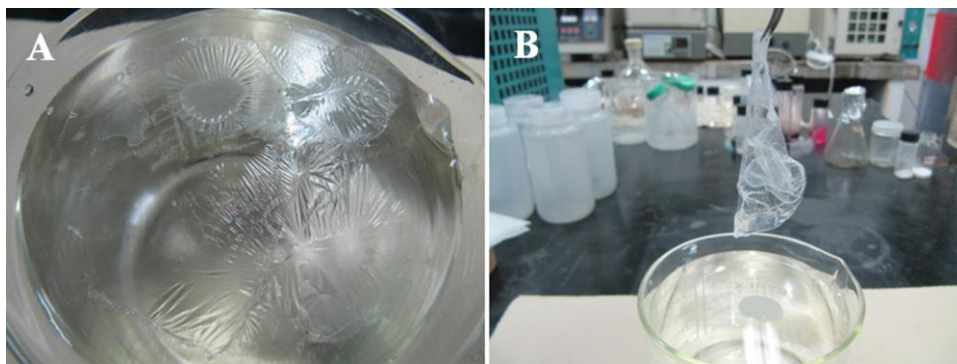


Fig. S16 Formation of the hydrophobic metallopolymer thin film on a water surface.

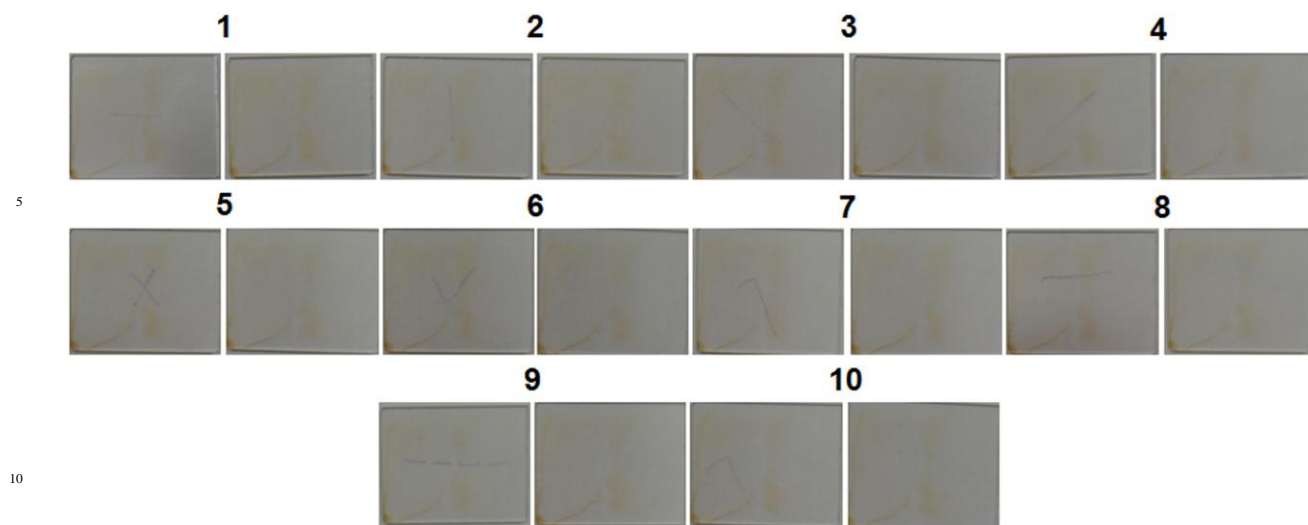


Fig. S17 Anti-stain coating of metallopolymer (PVCFeS-SiSH (SiSH-0.05 phr)) coated on a glass substrate (water based pen - (1-10 times of writing and erasing test)) and cured at 150 °C for 24 h.

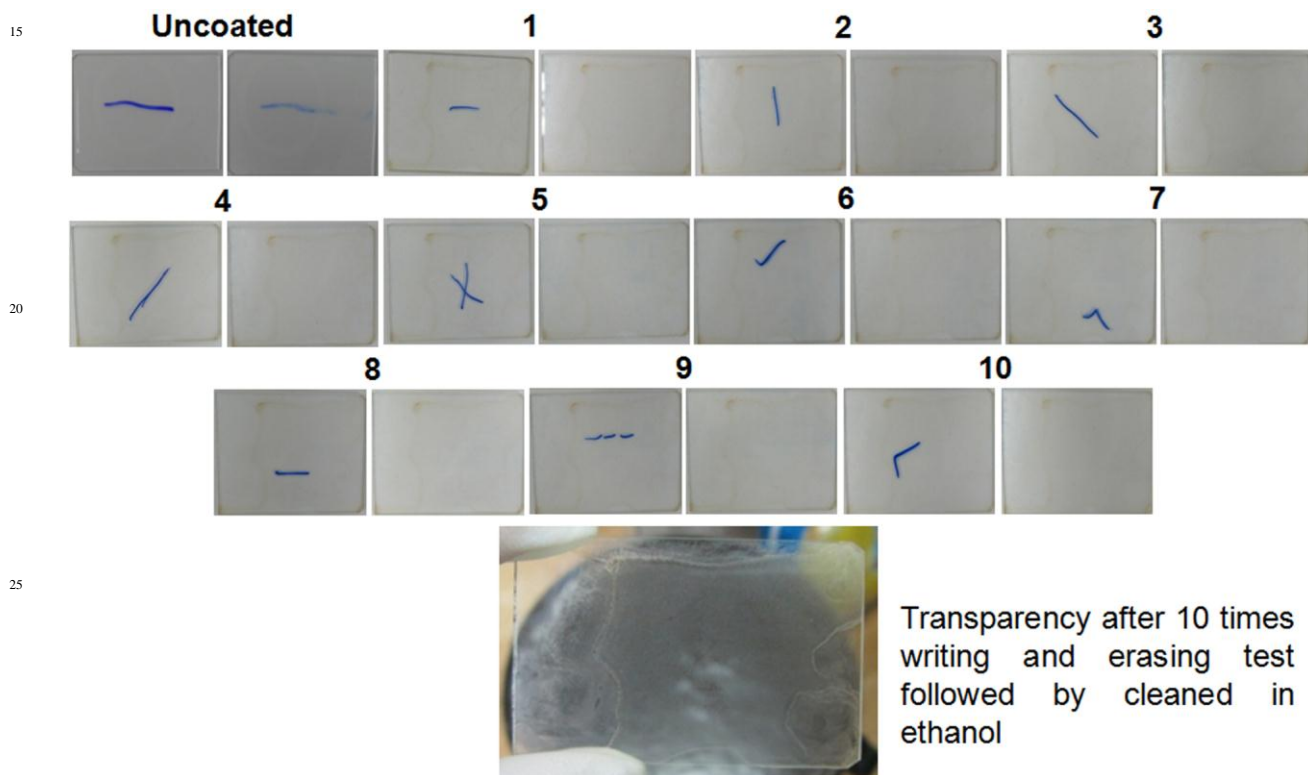
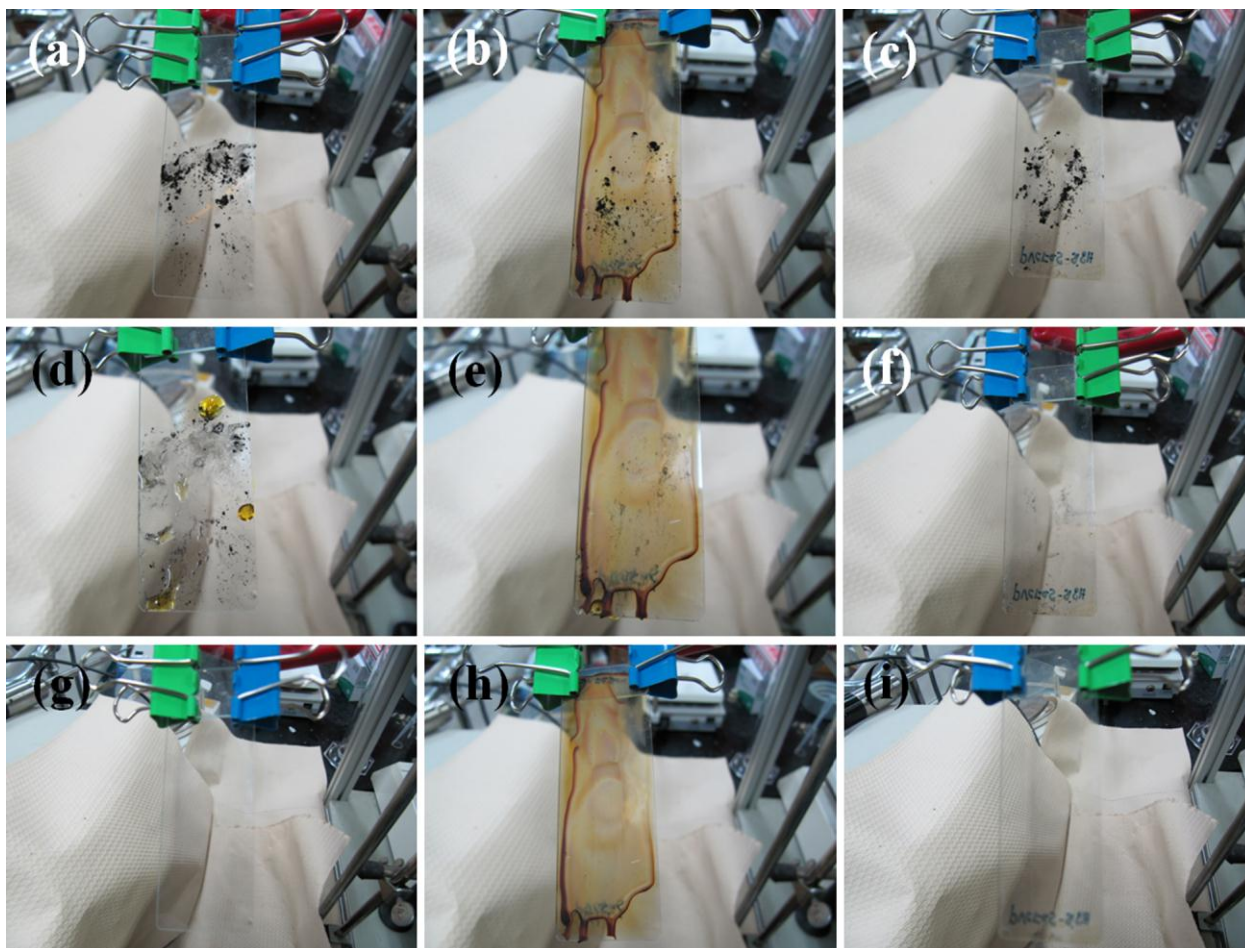


Fig. S18 Anti-stain coating of uncoated glass and metallopolymer (PVCFeS-SiMe (SiMe-0.01 phr)) coated on a glass substrate (oil based pen - (1-10 times writing and erasing test)) and cured at 150 °C for 24 h.

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20 **Fig. S19** Self-cleaning properties of a glass substrate, and PVCFeS metallopolymer and PVCFeS-SiSH (SiSH-0.05 phr) metallopolymer substrates coated on a glass. (a-c) Optical images of the substrates such as a glass, PVCFeS metallopolymer and PVCFeS-SiSH (SiSH-0.05 phr) metallopolymer coated substrates spread with activated charcoal powder. (d-f) Self-cleaning properties and their optical images of the substrates by dropped water droplets on the substrate (water colored with methyl orange
25 for visual purposes). (g-i) Optical images of the substrates after cleaned with a tissue paper.

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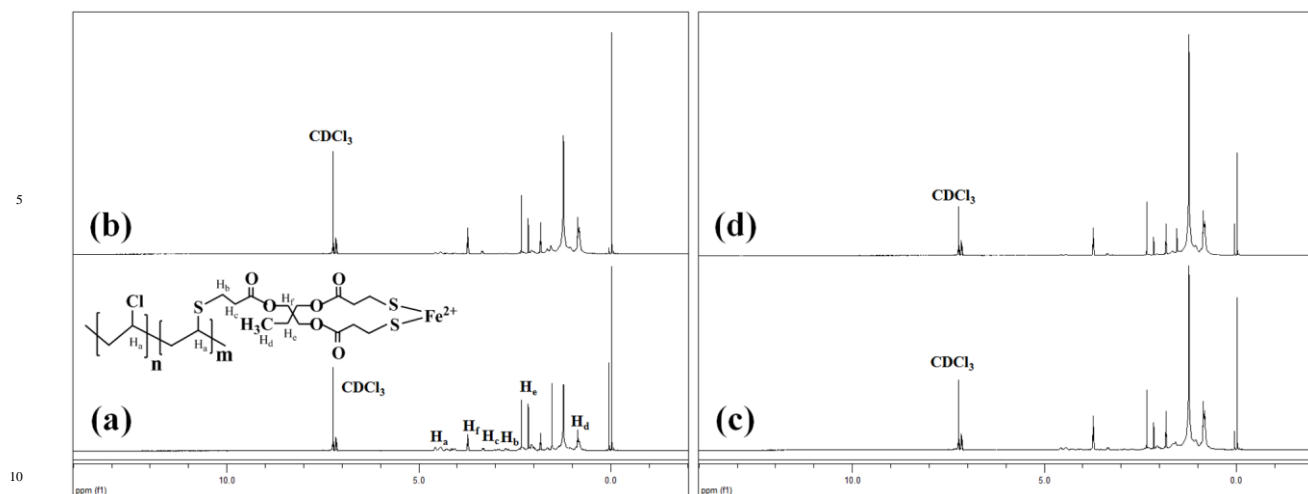


Fig. S20 $^1\text{H-NMR}$ spectra of PVCFeS metallopolymer solutions prepared with various contents of metal ions ((a) 0.1081 g, (b) 0.2162 g, (c) 0.3243 g and (d) 0.4324 g).

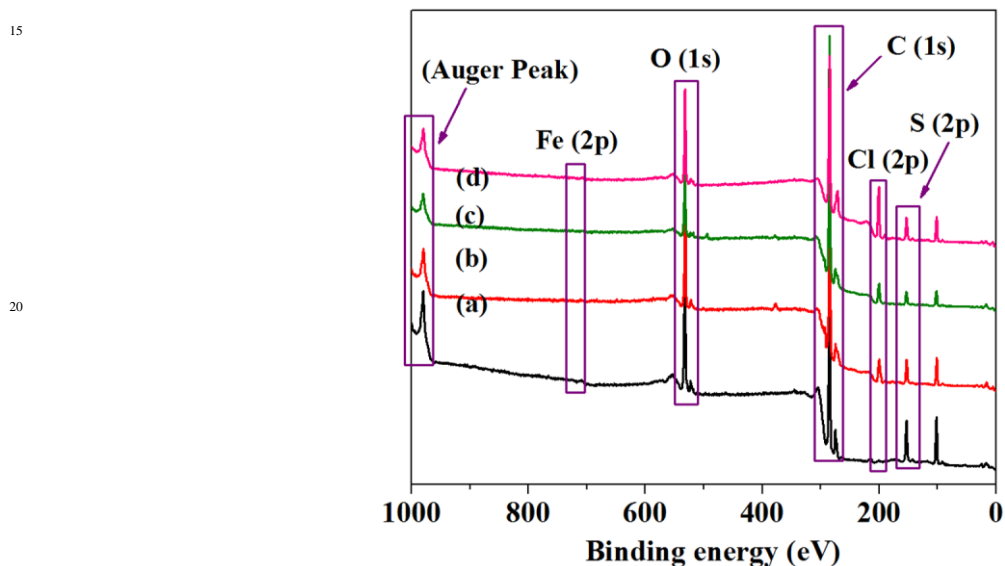


Fig. S21 XPS spectra of PVCFeS metallopolymer solutions prepared with various contents of metal ions ((a) 0.1081 g, (b) 0.2162 g, (c) 0.3243 g and (d) 0.4324 g).

Table S1. SCA of PVCFeS and PVCFeS-SiSH (SiSH-0.05 phr) metallopolymer substrates with increasing the thickness through the increase of spin coating time 1 to 4 times (SC1 to SC4) on the same substrate.

Sample	SCA for water (degree)	
	150 °C	150 °C
PVCFeS-1SC	143.27 ± 2.0	94.50 ± 3.0
PVCFeS-2SC	144.5 ± 1.8	102.33 ± 5.0
PVCFeS-3SC	145.43 ± 2.0	108.67 ± 3.4
PVCFeS-4SC	148.28 ± 2.5	110.07 ± 4.0
PVCFeS-SiSH 1SC (SiSH-0.05 phr)	112.20 ± 1.0	69.85 ± 3.0
PVCFeS-SiSH 2SC (SiSH-0.05 phr)	111.10 ± 1.0	80.70 ± 2.0
PVCFeS-SiSH 3SC (SiSH-0.05 phr)	109.33 ± 1.0	82.75 ± 2.5
PVCFeS-SiSH 4SC (SiSH-0.05 phr)	108.48 ± 1.0	83.05 ± 2.0

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Table S2. SCA (water) to PVC and PVCFeS Metallopolymer films prepared before and after washing (BW and AW) in deionised water.

Sample	SCA for water (degree)	
	40 °C	80 °C
PVC	-	107.27 ± 1.0
PVCFeS-BW	105.40 ± 2.0	112.30 ± 3.0
PVCFeS-AW	105.38 ± 2.0	100.33 ± 4.0

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Table S3. XPS chemical composition values of the PVCFeS metallopolymers prepared with various ratio of metal ions.

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Name	Binding energy (eV)	Metal ions ratio to PVCFeS metallopolymer			
		(0.11 g)	(0.22 g)	(0.32 g)	(0.43 g)
		At. Wt %	At. Wt %	At. Wt %	At. Wt %
C (1s)	285	84.93	86.07	81.75	73.59
O (1s)	533	14.19	9.19	12.71	13.95
Cl (2p)	201	0.41	4.21	4.96	11.61
S (2p)	164	0.38	0.35	0.38	0.49
Fe (2p)	708	0.1	0.18	0.2	0.37

Table S4. SCA of PVCFeS metallopolymer substrate prepared with various metal ions ratio (0.11 g-0.43 g) followed by spin coating and curing the surface at 80 °C and 150 °C.

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Sample	SCA for water (degree)		SCA for MI (degree)	
	80 °C	150 °C	80 °C	150 °C
PVCFeS-0.11 g	142.65 ± 3.0	143.27 ± 2.0	92.87 ± 2.2	94.50 ± 3.0
PVCFeS-0.22 g	108.10 ± 2.5	109.20 ± 2.5	52.05 ± 2.0	80.52 ± 3.0
PVCFeS-0.32 g	102.33 ± 1.0	108.70 ± 2.0	51.55 ± 3.0	79.65 ± 2.4
PVCFeS-0.43 g	98.43 ± 3.0	107.70 ± 2.0	45.93 ± 3.0	47.60 ± 3.0

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Movie S1wmv

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Movie S1. Self-cleaning properties of spin coated PVCFeS metallopolymer and PVCFeS-SiSH (SiSH-0.05 phr) metallopolymer substrates on a glass.

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