Supplementary Information (SI) for RSC Advances.

Synthesis, mixed-spin-state structure and Langmuir-Blodgett deposition of amphiphilic Fe(III) quinolylsalicylaldimine complexes

Peeranuch Poungsripong,[b] Theerapoom Boonprab,[a] Phimphaka Harding,[a] Keith S. Murray,[c] Wasinee Phonsri,[c] Ningjin Zhang[d], Jonathan A. Kitchen[e†] and David J. Harding[a†]

[a] School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand

Previous address: Functional Materials and Nanotechnology Centre of Excellence, Walailak University, Thasala, Nakhon Si Thammarat, 80160, Thailand

[b] Functional Materials and Nanotechnology Centre of Excellence, Walailak University, Thasala, Nakhon Si Thammarat, 80160, Thailand

[c] School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

[d] School of Chemistry, University of Southampton, Highfield, Southampton, SO17 3SJ, United Kingdom

[e] Department of Chemistry, Auckland University of Technology, New Zealand.

[f] The MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand

E-mail: david@g.sut.ac.th or jonathan.kitchen@aut.ac.nz

Contents

Synthesis of the pre-ligands and Hqsal-OR; R = $C_{12}H_{25}$, $C_{16}H_{33}$ and $C_{22}H_{45}$ _____ *1*

NMR spectra of Hqsal-OR; R = $C_{12}H_{25}$, $C_{16}H_{33}$ and $C_{22}H_{45}$ _____ *5*

FT-IR and UV-Visible absorption spectra of Hqsal-OR _____ *8*

Mass spectra of Hqsal-OR and $[Fe(qsal\text{-}OR)_2]NO_3$ (1-3) _____ *9*

FT-IR and UV-Visible absorption spectra of $[Fe(qsal\text{-}OR)_2]NO_3$ (1-3) _____ *13*

Crystallographic data for Hqsal-$OC_{12}H_{25}$ and 1 _____ *14*

Powder X-ray diffraction (PXRD) of $[Fe(qsal\text{-}OR)_2]NO_3$ (1,3) _____ *18*

Langmuir data for Hqsal-OR and [Fe(qsal-OR)2]NO_3 (1,3) _____ *18*

Synthesis of the pre-ligands and Hqsal-OR; R = $C_{12}H_{25}$, $C_{16}H_{33}$ and $C_{22}H_{45}$

The alkoxysalicyladehydes were synthesized using the procedure described by Albrecht and co-workers (C. Gandolfi, C. Moitzi, P. Schurtenberger, G. G. Morgan and M. Albrecht, *J. Am. Chem. Soc.*, 2008, **130**, 14434–14435). We include details of these pre-ligands in the interests of completeness.

Synthesis of 4-(dodecyloxy)salicylaldehyde

To a solution of 2,4-dihydroxybenzaldehyde (1.86 g, 13.2 mmol) in DMF (15 mL) was added $NaHCO_3$ (1.11 g, 13.2 mmol). After 10 min stirring at RT, 1-bromododecane (3.163 mL, 13.2 mmol) in THF (20 mL) was slowly added. The mixture was heated to 120 °C for overnight under Ar. After cooling to RT, aqueous HCl (1 M, 100 mL) was added, and the mixture was stirred vigorously and then filtered. Purification by column chromatography (SiO_2, hexane-ethyl acetate 9:1) afforded a micro analytically pure white solid (2.71 g, 67%). ν_{max}/cm^{-1} 3053, 2919 (alkyl chain), 2852 (alkyl chain), 1673 (C=O).

Synthesis of 4-(hexyloxy)salicylaldehyde

To a solution of 2,4-dihydroxybenzaldehyde (1.86 g, 13.2 mmol) in DMF (20 mL) was added $NaHCO_3$ (1.11 g, 13.2 mmol). After 10 min stirring at RT, 1-bromohexadecane (4.0305 mL, 13.2 mmol) in THF (20 mL) was slowly added. The mixture was heated to 120 ◦C for overnight under Ar. After cooling to RT, aqueous HCl (1 M, 100 mL) was added until pH ≈ 7, and the mixture was stirred vigorously and then cooled in the fridge. The residue was suspended, filtered to give the title compound as a pale-cream solid (3.57 g, 74%). ν_{max}/cm^{-1} 3057, 2920 (alkyl chain), 2851 (alkyl chain), 1671 (C=O).

Synthesis of 4-(docoxyloxy)salicylaldehyde

To a solution of 2,4-dihydroxybenzaldehyde (1.86 g, 13.2 mmol) in DMF (20 mL) was added $NaHCO_3$ (1.11 g, 13.2 mmol). After 10 min stirring at RT, 1-bromodocosane (4.50 g, 11.0 mmol) in DMF–THF (1:4 v/v, 25 mL) was slowly added. The mixture was heated to 120 ◦C for overnight under Ar. After cooling to RT, aqueous HCl (1 M, 100 mL) was added about 10 mL, and the mixture was stirred vigorously and then filtered. The residue was suspended in acetone (50 mL), filtered, dissolved solid in THF (250 mL), and then left overnight. A brownish precipitate was filtered off. The solution was evaporated and EtOH was added, giving pale-purple powder. The pale-purple powder was dissolved in warm THF (20 mL), cooled in the fridge, and then filtered to give a pale-grey solid (3.26 g, 55%). ν_{max}/cm^{-1} 3055, 2918 (alkyl chain), 2851 (alkyl chain), 1676 (C=O).

Synthesis of Hqsal-$OC_{12}H_{25}$

To a solution of 4-(dodecyloxy)salicylaldehyde (1.22 g, 4.0 mmol) in DCM (10 mL) was added 8-aminoquinoline (0.57 g, 4.0 mmol). Then a few drops of trifluoroacetic acid were added to the solution. The solution was stirred overnight under nitrogen, and then evaporated to dryness (yellow solid). This solid was washed with hexane and diethyl-ether to give the title compound as a yellow solid (1.43 g, 83%). HRMS (ESI+) *m/z* 433.2848 $[M+H]^+$ (Calcd. for $C_{28}H_{37}N_2O_2$, 433.2850). 11.48 (1H, s, imine C*H*), 9.70 (1H, d, J=0.48 Hz, O*H*), 8.82 (1H, dd, J=6.00, 2.60, Ar_q-C*H*), 8.14 (1H, dd, J=8.28, 1.64 Hz, Ar_q-C*H*), 7.41 (2H, m, Ar_q-C*H*), 7.36 (1H, d, J=7.68 Hz, Ar_q-C*H*), 7.18 (1H, dd, J=8.16, 1.16 Hz, Ar_q-C*H*), 6.97 (1H, dd, J=7.54, 1.18 Hz, Ar_s-C*H*), 6.53 (1H, dd, J=8.68, 2.32 Hz, Ar_s-C*H*), 6.41 (1H, d, J=2.32 Hz, Ar_s-C*H*), 4.00 (2H, t, J=6.56 Hz, OCH_2), 1.78 (2H, m, OCH_2CH_2), 1.44 (2H, m, $OCH_2CH_2CH_2$), 1.26 (16H, m, 18 x alkyl-chain CH_2), 0.88 (3H, t, J=13.84 Hz, CH_2CH_3). ν_{max}/cm^{-1} 3061, 2921 (alkyl chain), 2850 (alkyl chain), 1622 (C=N).

Synthesis of Hqsal-$OC_{16}H_{33}$

To a solution of 4-(hexyloxy)salicylaldehyde (0.75 g, 2.0 mmol) in DCM (10 mL) was added 8-aminoquinoline (0.29 g, 2.0 mmol). Then a few drops of trifluoroacetic acid were added to the solution. The solution was stirred overnight under nitrogen, and then evaporated to dryness (yellow solid). This solid was washed with hexane and diethyl-ether to give the title compound as a yellow solid (0.87 g, 90%). HRMS (ESI+) *m/z* 489.3482 $[M+H]^+$ (Calcd. for $C_{32}H_{45}N_2O_2$, 489.3476). 11.48 (1H, s, imine C*H*), 9.70 (1H, d, J=0.44 Hz, O*H*), 8.78 (1H, dd, J=4.18, 1.70, Ar_q-C*H*), 8.10 (1H, dd, J=8.32, 1.68 Hz, Ar_q-C*H*), 7.39 (2H, m, Ar_q-C*H*), 7.34 (1H, d, J=7.56 Hz, Ar_q-C*H*), 7.16 (1H, dd, J=8.14, 1.18 Hz, Ar_q-C*H*), 6.95 (1H, dd, J=7.48, 1.24 Hz, Ar_s-C*H*), 6.53 (1H, dd, J=8.66, 2.34 Hz, Ar_s-C*H*), 6.41 (1H, d, J=2.04 Hz, Ar_s-C*H*), 4.00 (2H, t, J=6.58 Hz, OCH_2), 1.79 (2H, m, OCH_2CH_2), 1.45 (2H, m, $OCH_2CH_2CH_2$), 1.25 (24H, m, 18 x alkyl-chain CH_2), 0.88 (3H, t, J=13.74 Hz, CH_2CH_3). ν_{max}/cm^{-1} 3063, 2921 (alkyl chain), 2850 (alkyl chain), 1618 (C=N).

Synthesis of Hqsal-$OC_{22}H_{45}$

To a solution of 4-(docosyloxy)salicylaldehyde (0.89 g, 2.0 mmol) in DCM (10 mL) was added 8-aminoquinoline (0.29 g, 2.0 mmol). Then a few drops of trifluoroacetic acid were added to the solution. The solution was stirred overnight under nitrogen, and then evaporated to dryness (yellow solid). This solid was washed with hexane and diethyl-ether to give the title compound as a yellow solid (1.13 g, 99%). HRMS (ESI+) *m/z* 573.4413 $[M+H]^+$ (Calcd. for $C_{38}H_{57}N_2O_2$, 573.4415). δH(400 MHz; $CDCl_3$) 11.48 (1H, s, imine C*H*), 9.70 (1H, d, J=0.39 Hz, O*H*), 8.88 (1H, dd, J=4.39, 1.66, Ar_q-C*H*), 8.21 (1H, dd, J=8.34, 1.61 Hz, Ar_q-C*H*), 7.46 (1H, dd, 8.32, 4.41 Hz, Ar_q-C*H*), 7.40 (2H, m, Ar_q-C*H*), 7.21 (1H, dd, J=8.15, 1.14 Hz, Ar_q-C*H*), 6.99 (1H, dd, J=7.55, 1.18 Hz, Ar_s-C*H*), 6.52 (1H, dd, J=8.67, 2.32 Hz, Ar_s-C*H*), 6.41 (1H, d, J=2.28 Hz, Ar_s-C*H*), 4.00 (2H, t, J=6.57 Hz, OCH_2), 1.79 (2H, m, OCH_2CH_2), 1.44 (2H, m, $OCH_2CH_2CH_2$), 1.25 (36H, m, 18 x alkyl-chain CH_2), 0.88 (3H, t, J=13.74 Hz, CH_2CH_3). ν_{max}/cm^{-1} 3060, 2917 (alkyl chain), 2849 (alkyl chain), 1626 (C=N).

NMR spectra of Hqsal-OR; R = $C_{12}H_{25}$, $C_{16}H_{33}$ and $C_{22}H_{45}$

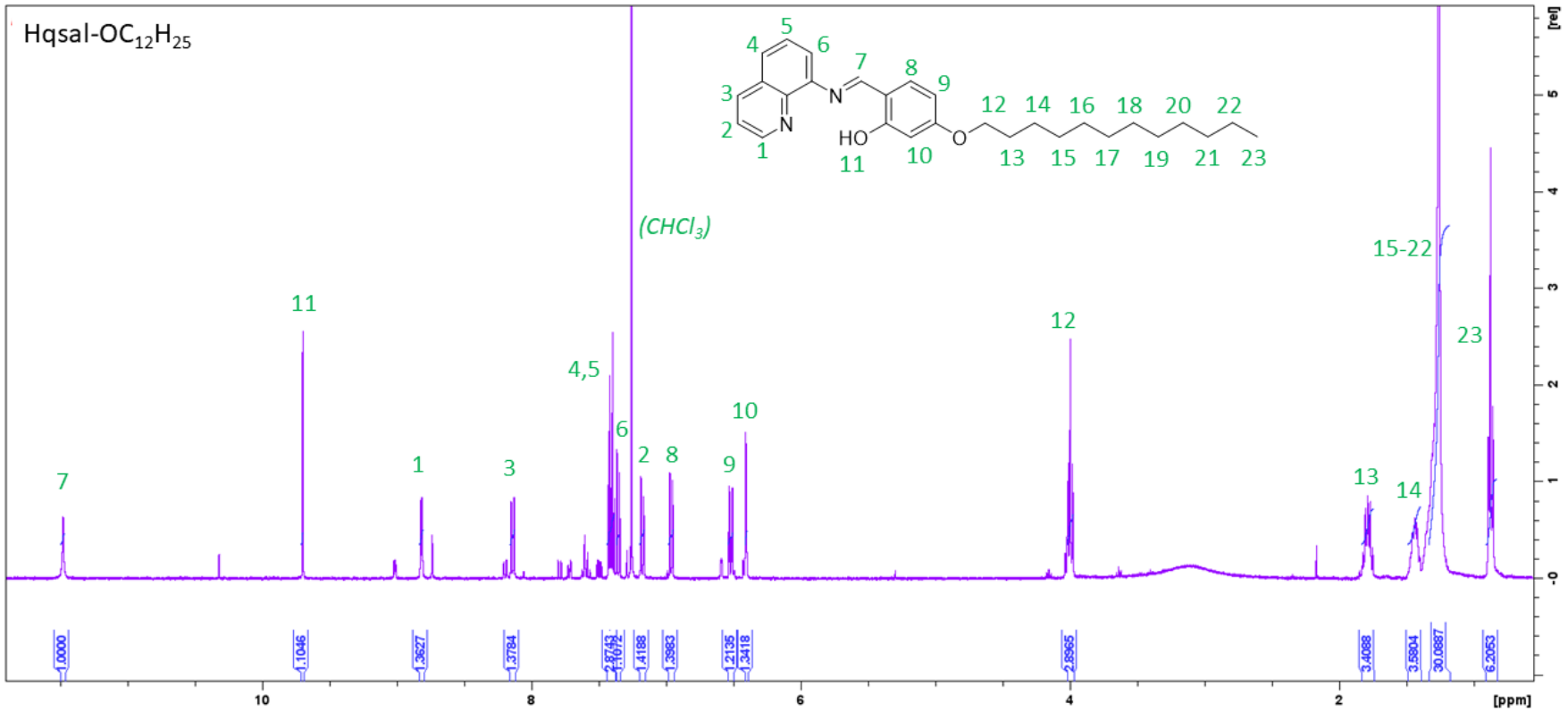


Figure S1 ^{1}H-NMR ($CDCl_3$) of Hqsal-$OC_{12}H_{25}$

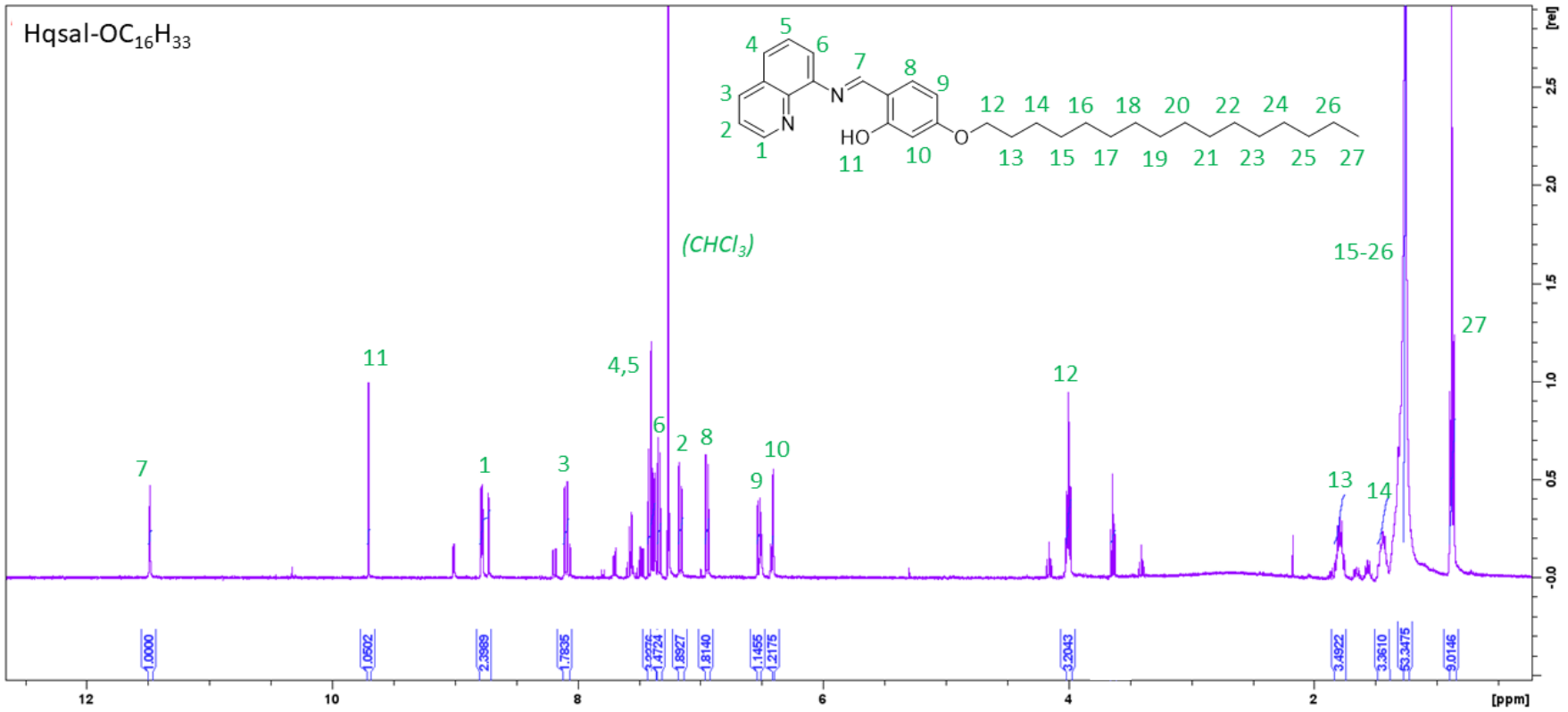


Figure S2 ^{1}H-NMR ($CDCl_3$) of Hqsal-$OC_{16}H_{33}$

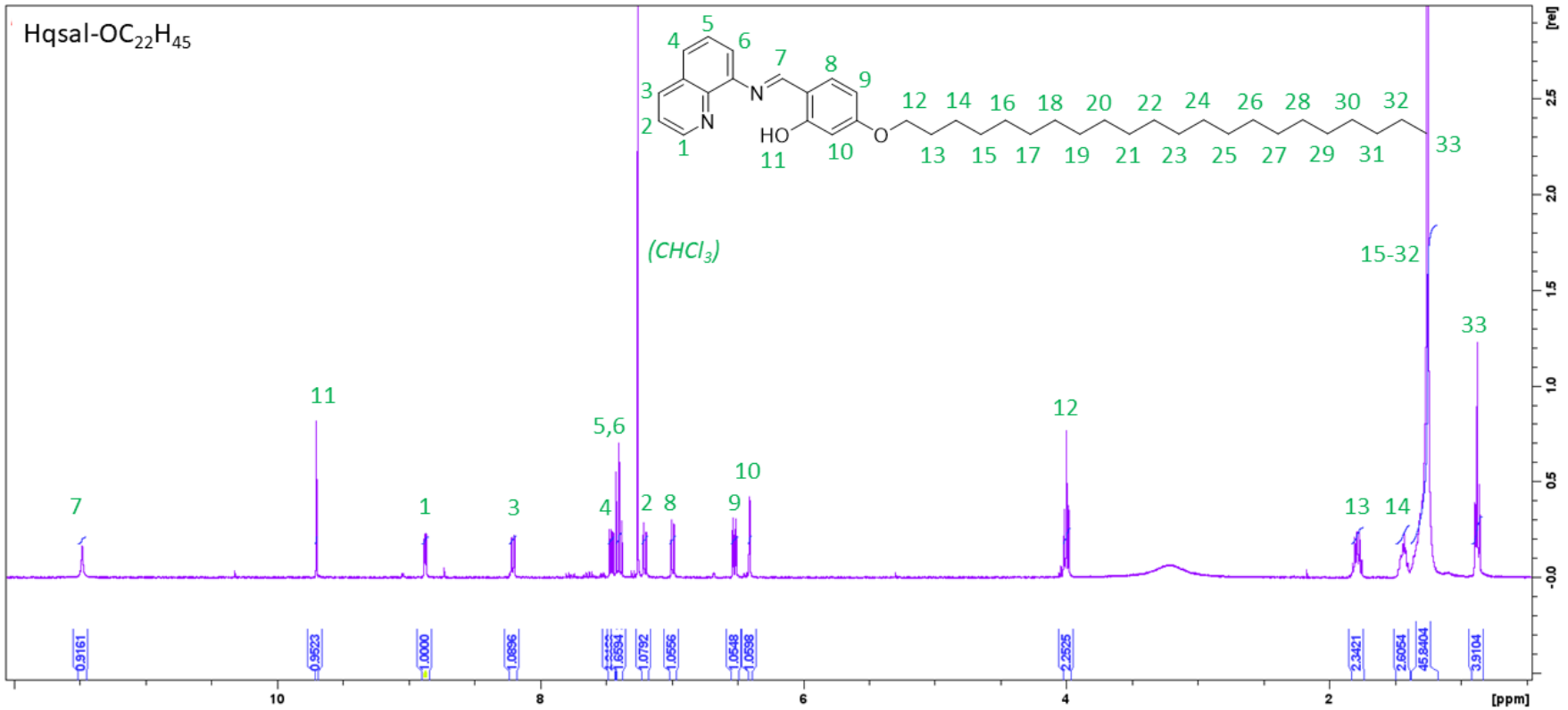


Figure S3 ^{1}H-NMR ($CDCl_3$) of Hqsal-$OC_{22}H_{45}$

FT-IR and UV-Visible absorption spectra of Hqsal-OR

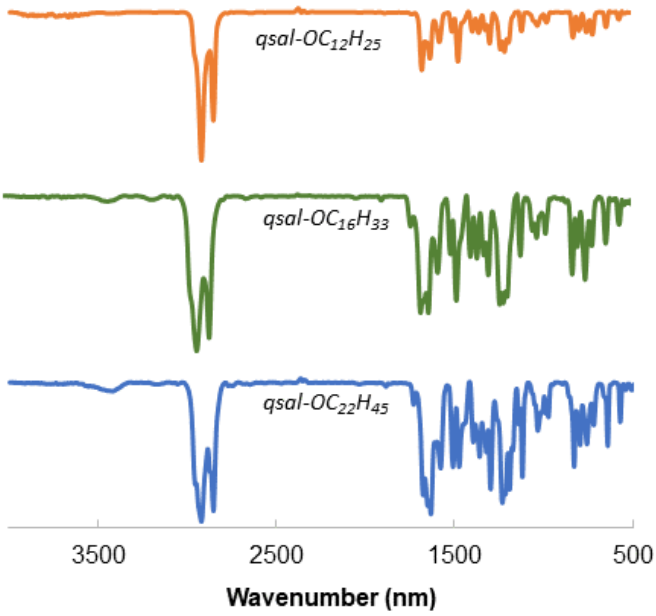


Figure S4 FT-IR spectra of Hqsal-OR ligands.

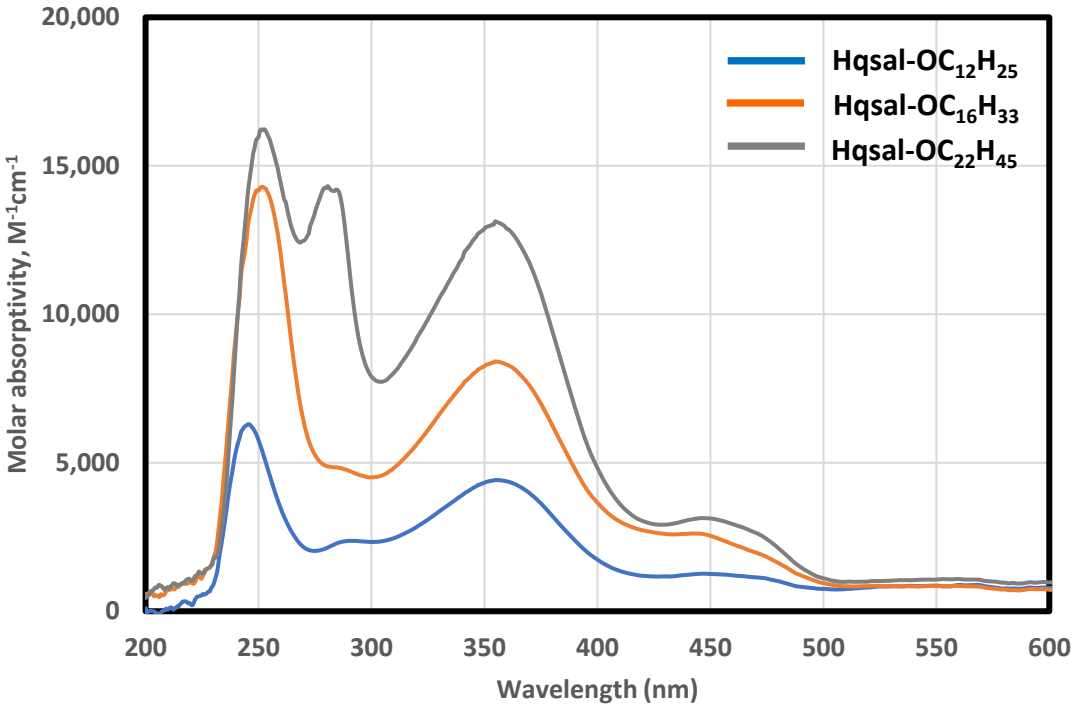


Figure S5 UV-Visible absorption spectra (MeOH, 0.0001 M) of Hqsal-OR ligands.

Mass spectra of Hqsal-OR and $[Fe(qsal\text{-}OR)_2]NO_3$ (1-3)

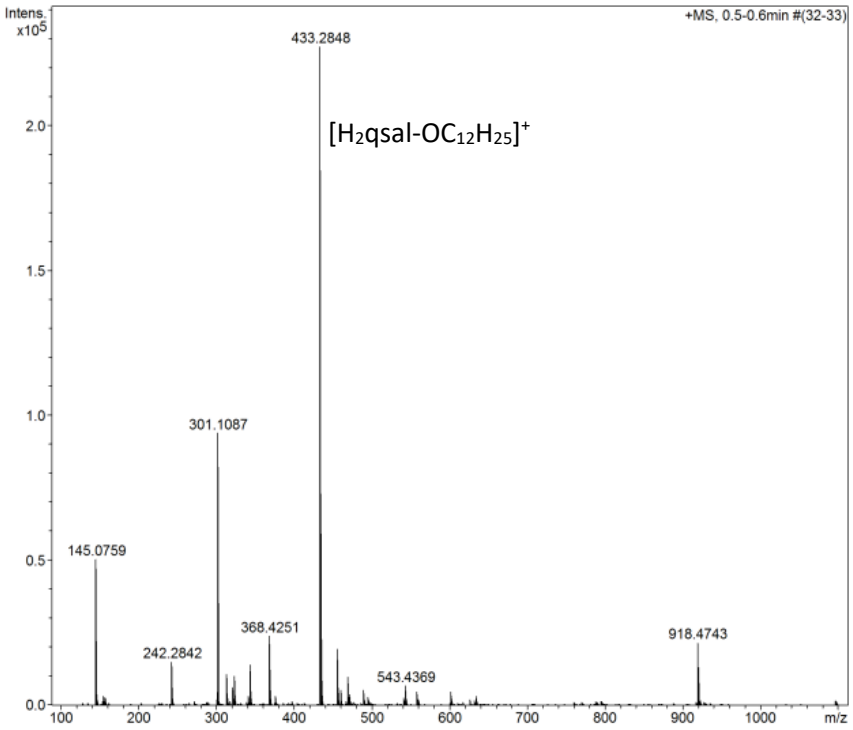


Figure S6 Mass spectrum (ESI+) of Hqsal-$OC_{12}H_{25}$

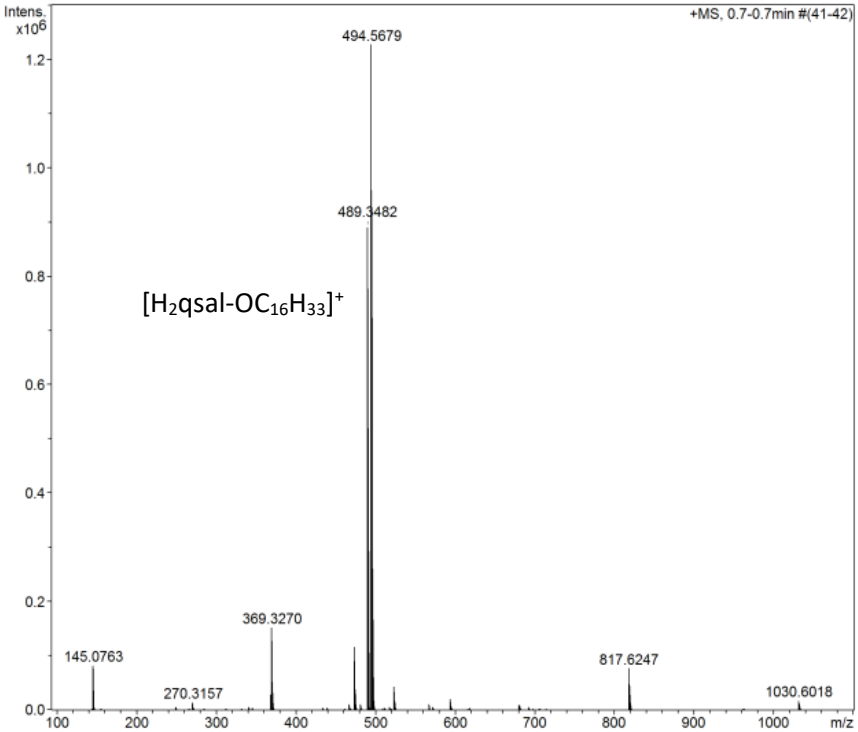


Figure S7 Mass spectrum (ESI+) of Hqsal-$OC_{16}H_{33}$

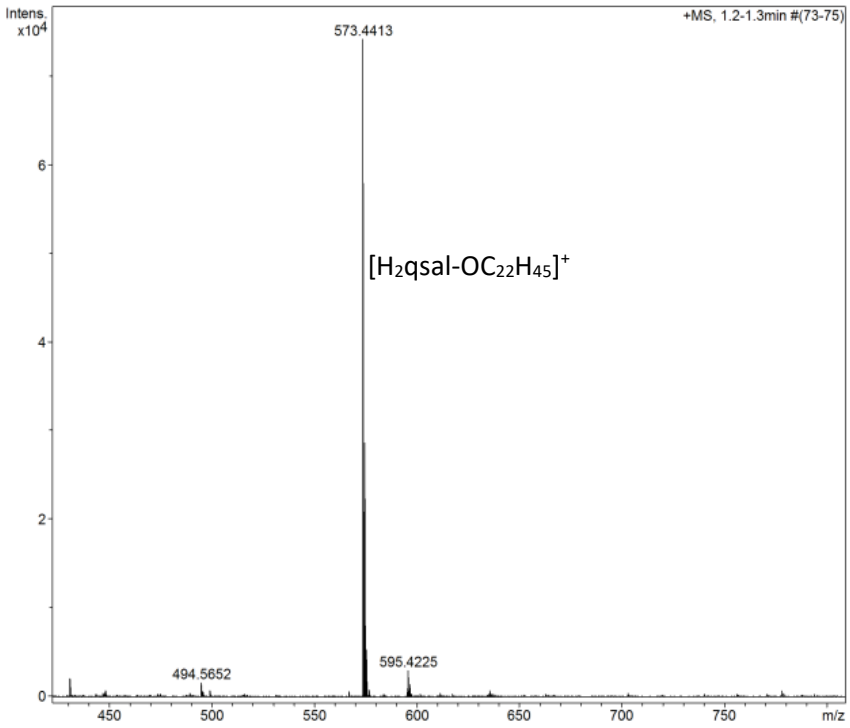


Figure S8 Mass spectrum (ESI+) of Hqsal-$OC_{22}H_{45}$

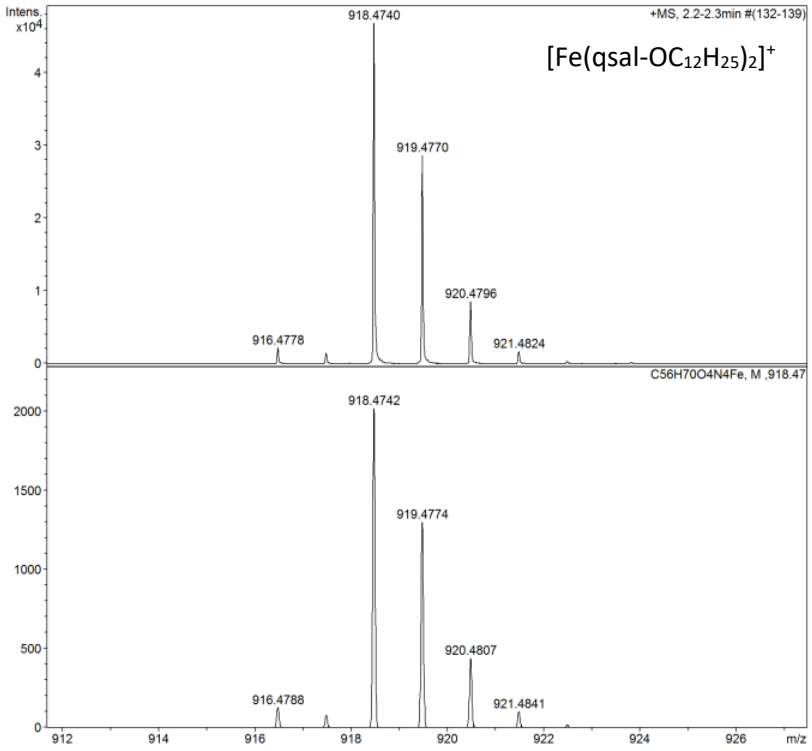


Figure S9 Observed (top) and calculated (bottom) isotope pattern (ESI+) of **1**

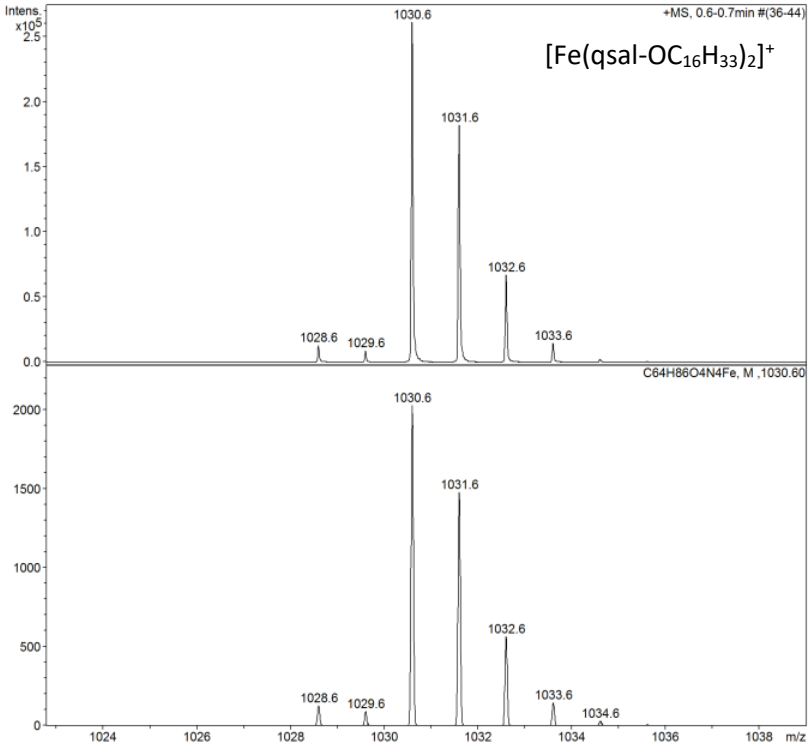


Figure S10 Observed (top) and calculated (bottom) isotope pattern (ESI+) of **2**

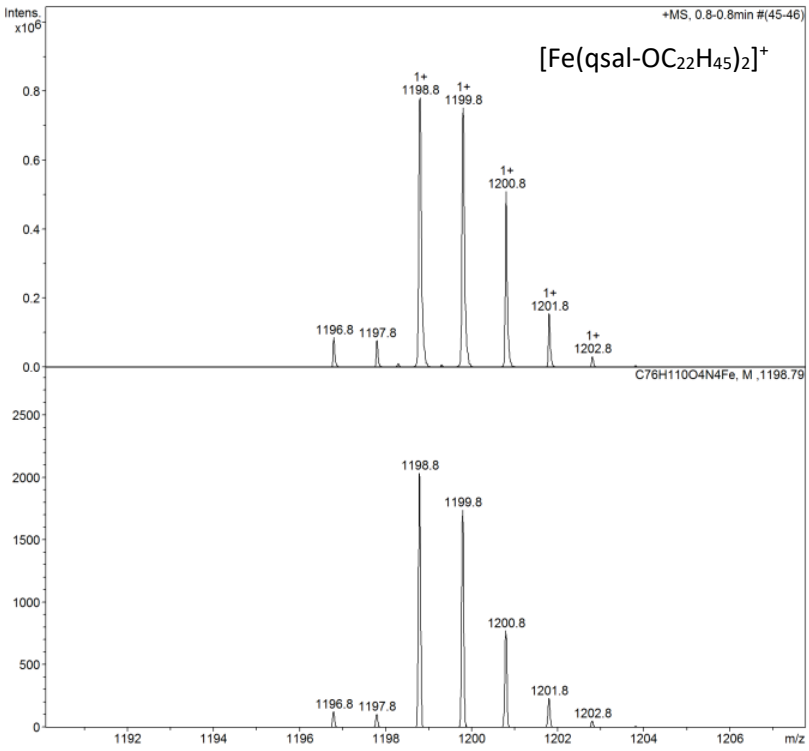


Figure S11 Observed (top) and calculated (bottom) isotope pattern (ESI+) of **3**

FT-IR and UV-Visible absorption spectra of $[Fe(qsal\text{-}OR)_2]NO_3$ (1-3)

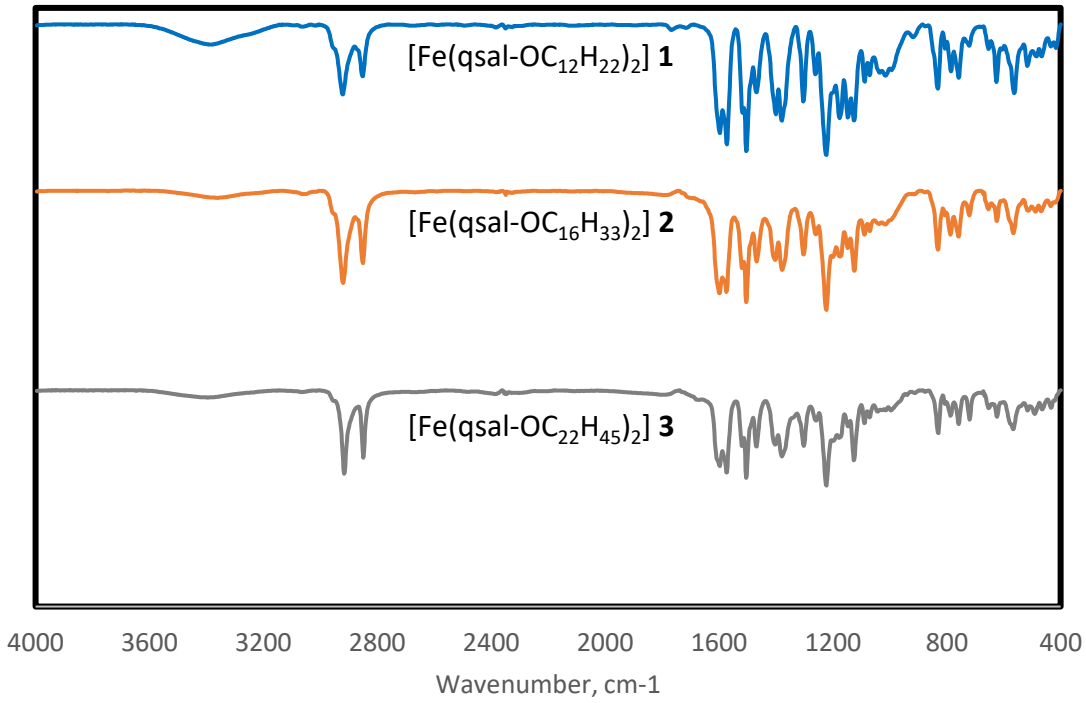


Figure S12 FT-IR spectra of **1**-**3**

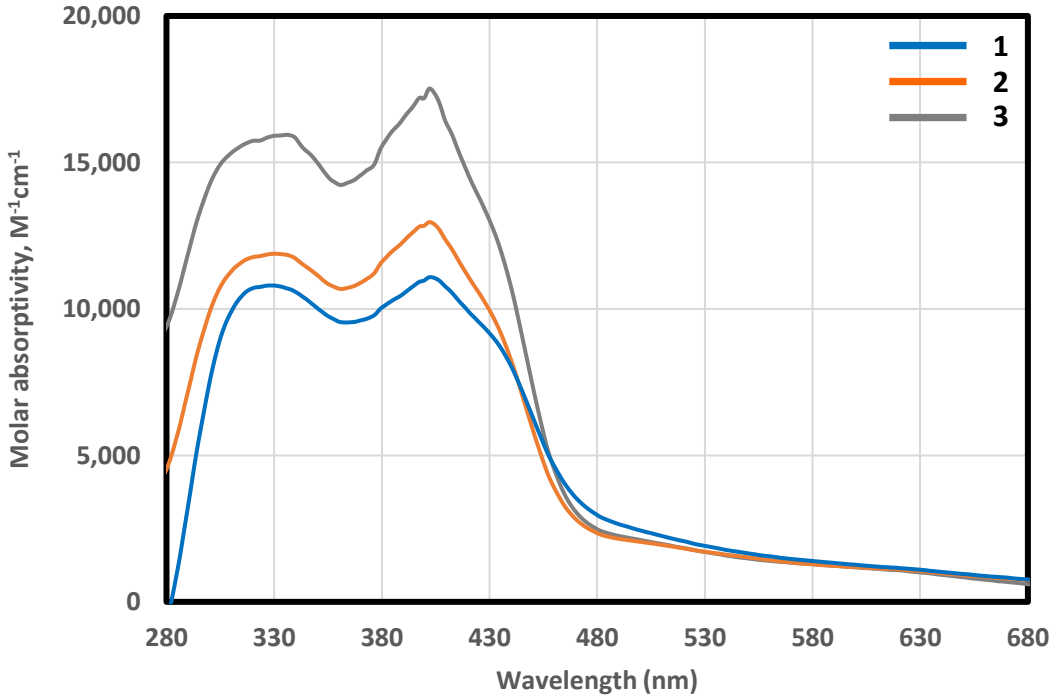


Figure S13 UV-Visible absorption spectra (MeOH, 0.0001 M) of **1**-**3**.

Crystallographic data for Hqsal-$OC_{12}H_{25}$ and 1

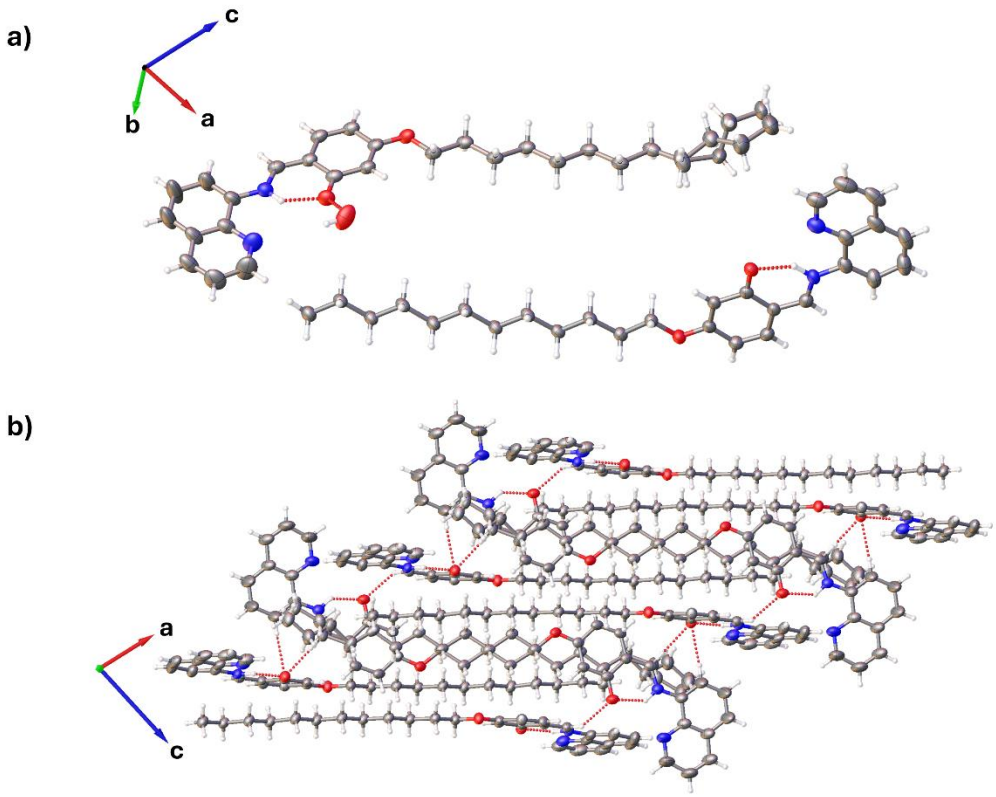


Figure S14 a) Asymmetric unit and b) packing diagram of Hqsal-$OC_{12}H_{25}$.

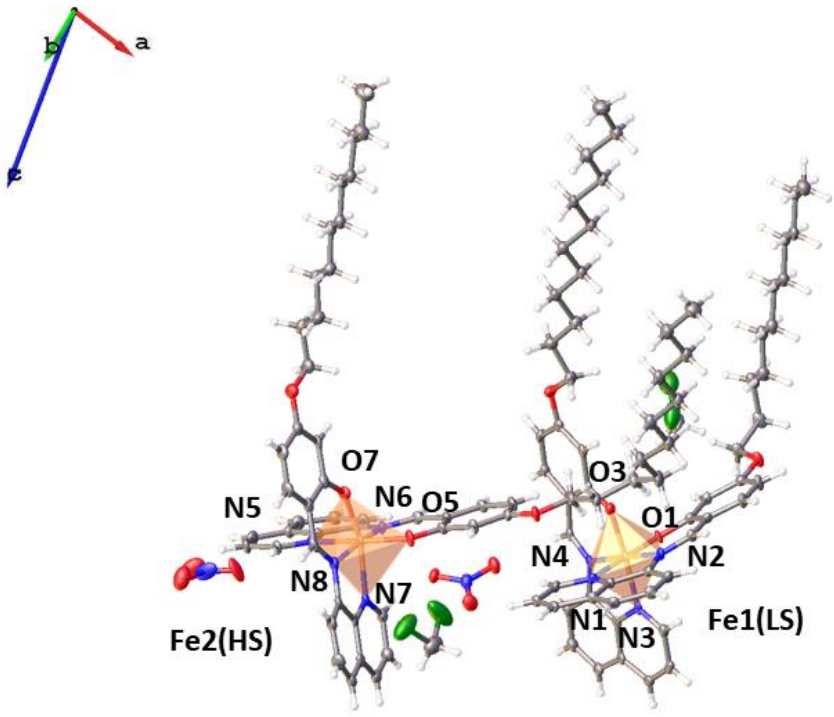


Figure S15 Asymmetric unit of **1**.

Table S1 Crystallographic data and refinement parameters for Hqsal-$OC_{12}H_{25}$ and **1**

	Hqsal-$OC_{12}H_{25}$	**1**
Formula	$C_{28}H_{36}N_2O_2 \cdot 2/3CH_3COOH \cdot 1/3H_2O$	$C_{56}H_{70}FeN_5O_7 \cdot CH_2Cl_2$
T (K)	293(2)	293(2)
MW (g/mol)	472.24	1065.94
Radiation	MoK/α	
λ (Å)	0.71073	
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.5229(3)	10.1979(3)
b (Å)	13.1254(3)	15.7859(6)
c (Å)	30.4202(6)	35.2696(11)
α (°)	95.812(2)	87.523(3)
β (°)	97.764(2)	83.973(3)
γ (°)	100.884(2)	72.534(3)
Cell volume ($Å^3$)	4053.30(17)	5385.7(3)
Z	18	4
μ (mm^{-1})	0.082	0.436
Reflections collected	18590	18922
Independent reflections, R_{int} (%)	13617, 3.85	12359, 7.09
R-Factor (%), wR_2 (%)	6.19, 15.66	7.86, 15.83
CCDC No.		

Table S2 Intermolecular interaction in Hqsal-$OC_{12}H_{25}$

Interaction	Distance (Å)
Intramolecular imine in keto form	
N2-H···O1	1.515
N4-H···O3	1.968
N6-H···O5	2.013
Solvent mediated intermolecular interaction	
O7-H···O1	1.515
O9-H···O3	1.426
C1-H···O11	2.638
C41-H···O5	2.508
C43-H···O9	2.647
C35-H···O10	2.493
C38-H···O10	2.368
C63-H···O1	2.636
C66-H···O7	2.371
C88-H···O8	2.639
O11-H···O5	1.602
O11-H···O9	2.058
π mediated intermolecular interaction	
π(sal)···π(quin)	3.364, 3.431
C47-H···π(sal)	3.480
C51-H···π(quin)	3.122, 3.227

Table S3 Fe-ligand bond lengths, angles and octahedral distortions parameters in $[Fe(qsal\text{-}OC_{12}H_{25})_2]NO_3$ **1**

Parameters	Fe1 (LS)	Fe2 (HS)
$Fe\text{-}O_{avg}$ (Å)	1.882	1.912
$Fe\text{-}N_{imine}$ (Å)	1.931	2.114
$Fe\text{-}N_{quin}$ (Å)	1.972	2.136
$Fe\text{-}N_{avg}$ (Å)	1.952	2.125
$Fe\text{-}O/N_{avg}$ (Å)	1.928	2.019
$\Delta Fe\text{-}O/N_{avg}$ (Å)	-	0.091
Σ (°)	49.6	71.1
Θ (°)	131	250
ΔΣ, ΔΘ (°)	-	21.5, 119

Table S4 Intermolecular interaction in $[Fe(qsal\text{-}OC_{12}H_{25})_2]NO_3$ **1**

Interaction	Distance (Å)
Interaction between 2 Fe center and corresponding nitrate and CH_2Cl_2	
$\pi_{quin}\cdots\pi_{sal}$	4.382
C89-H$\cdots\pi_{quin}$	2.961
C90-H$\cdots\pi_{quin}$	2.951
C68-H$\cdots\pi_{sal}$	3.334
C69-H$\cdots$O3	3.004
C101-H$\cdots$O6	2.740
C1-H$\cdots$O10	2.496
C2-H$\cdots$O9	2.493
C73-H$\cdots$O11	2.669
C57-H$\cdots$O14	2.647
C58-H$\cdots$O12	2.537
C113-H$\cdots$O3	3.036
C113-H$\cdots\pi_{sal}$	2.678
C36-H$\cdots$Cl1	3.144
C45-H$\cdots$Cl1	3.260
C91-H$\cdots$Cl2	3.471
O5$\cdots$Cl3	3.501
C114-H$\cdots$O13	2.515
Interaction between Fe center in the *2*-D plane with same type of Fe center	
C7-H$\cdots$O4	2.770
C10-H$\cdots$O4	2.770
$\pi_{quin}\cdots\pi_{quin}$	3.886
Interaction between *2*-D plane mediated by nitrate and CH_2Cl_2	
C74-H$\cdots$O9	2.572
C18-H$\cdots$O10	2.612
C59-H$\cdots$O11	2.557
C73-H$\cdots$O11	2.669
C74-H$\cdots$O11	2.618
C75-H$\cdots$O11	2.538
C21-H$\cdots$O12	2.576
C114-H$\cdots$O12	2.515
C23-H$\cdots$O13	2.497
C26-H$\cdots$O13	2.441
C26-H$\cdots$O14	2.756
Interaction between 2 bilayer linked by CH_2Cl_2	
C100-H$\cdots$Cl2	3.059
Fe-Fe distances in the *2*-D plane	
Fe1$\cdots$ Fe1	10.198, 12.877
Fe2$\cdots$ Fe2	10.198, 10.209
Fe1$\cdots$ Fe1 (across bilayer)	25.298
Fe2$\cdots$ Fe2 (across bilayer)	28.865

Powder X-Ray diffraction (PXRD) of $[Fe(qsal\text{-}OR)_2]NO_3$ (1-3)

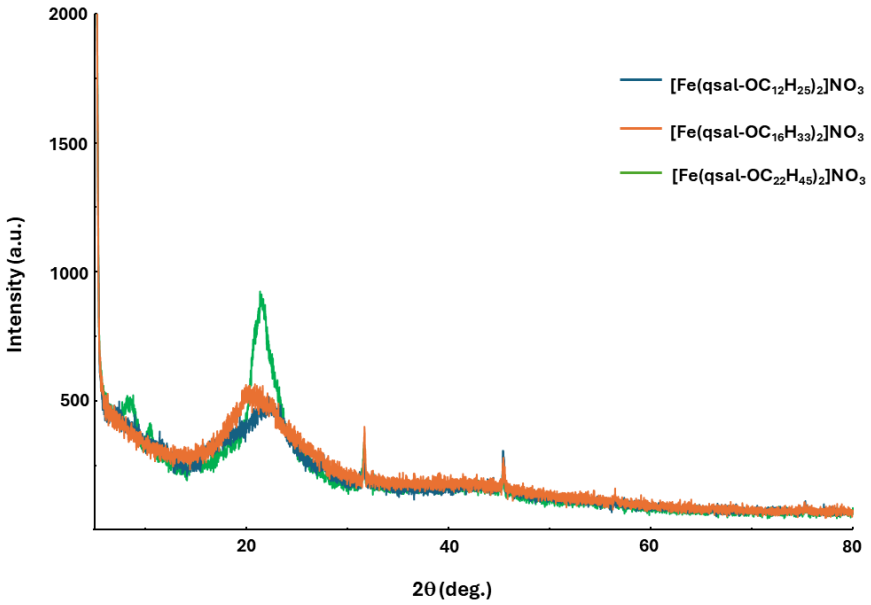


Figure S16 PXRD patterns of **1**-**3**.

Langmuir data for Hqsal-OR and $[Fe(qsal\text{-}OR)_2]NO_3$ (1-3)

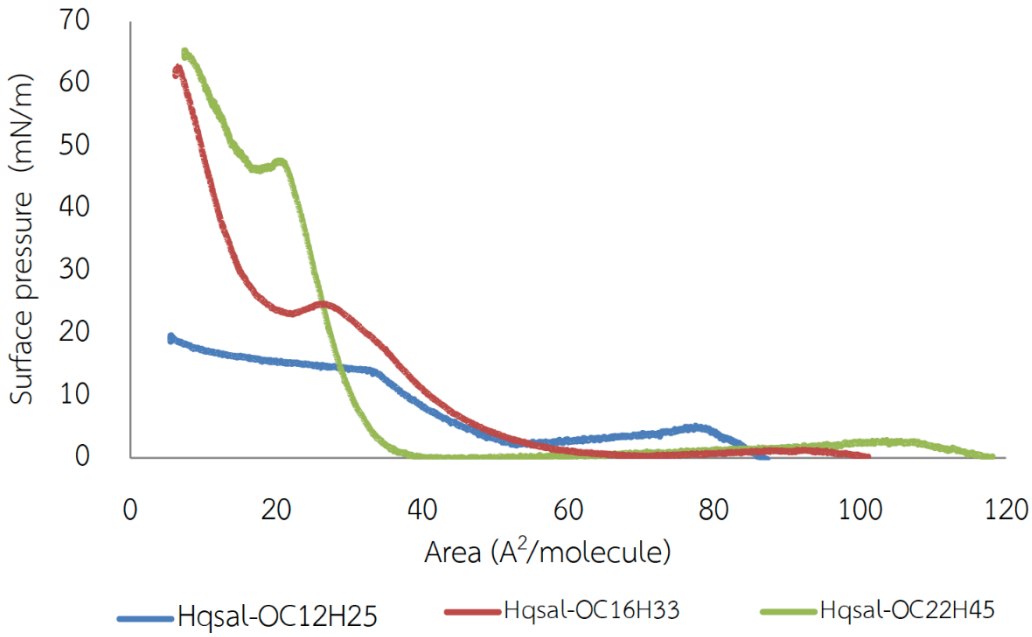


Figure S17 Pressure-area isotherms for ligands Hqsal-OR.

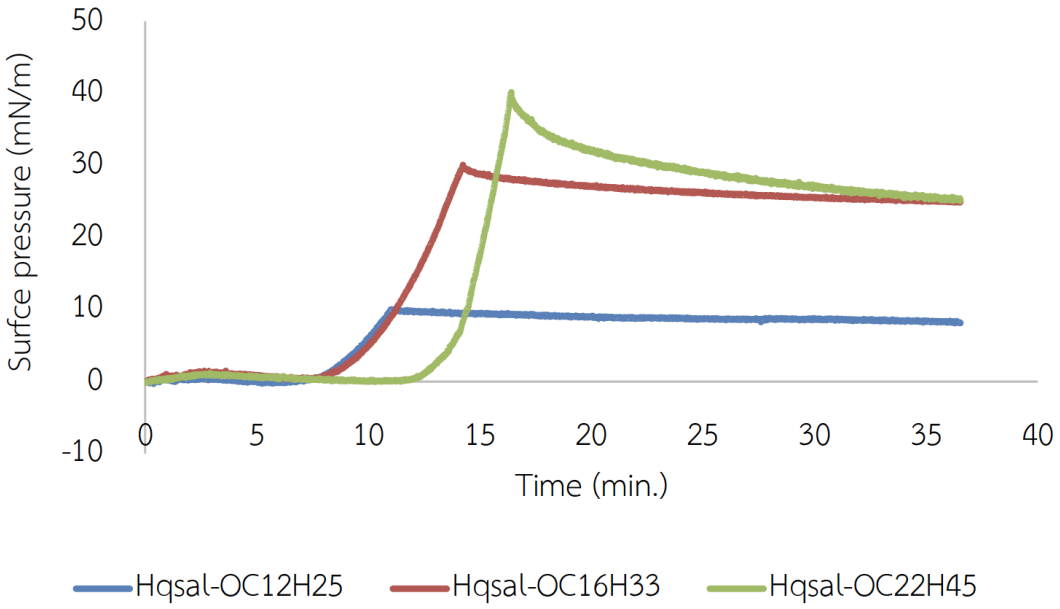
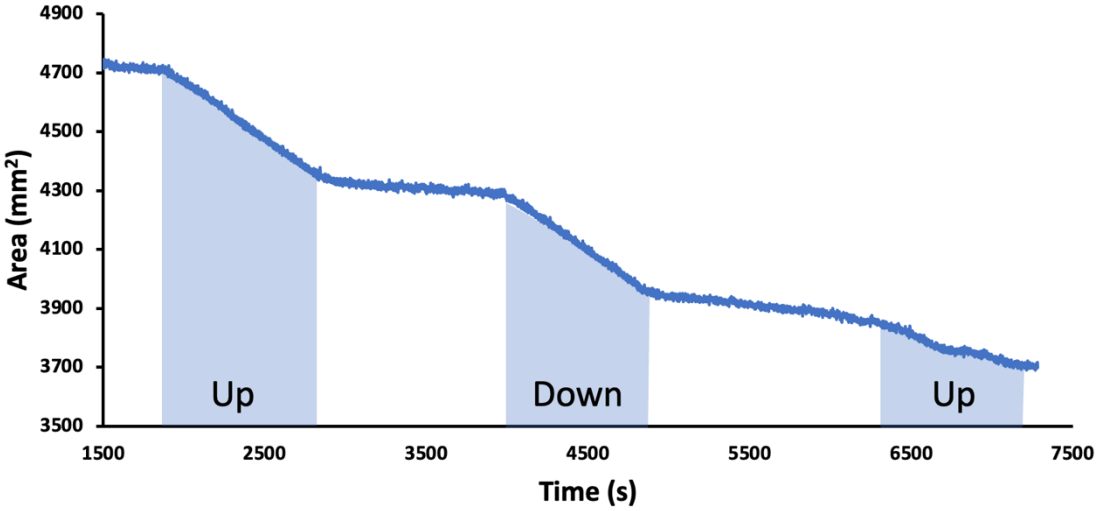
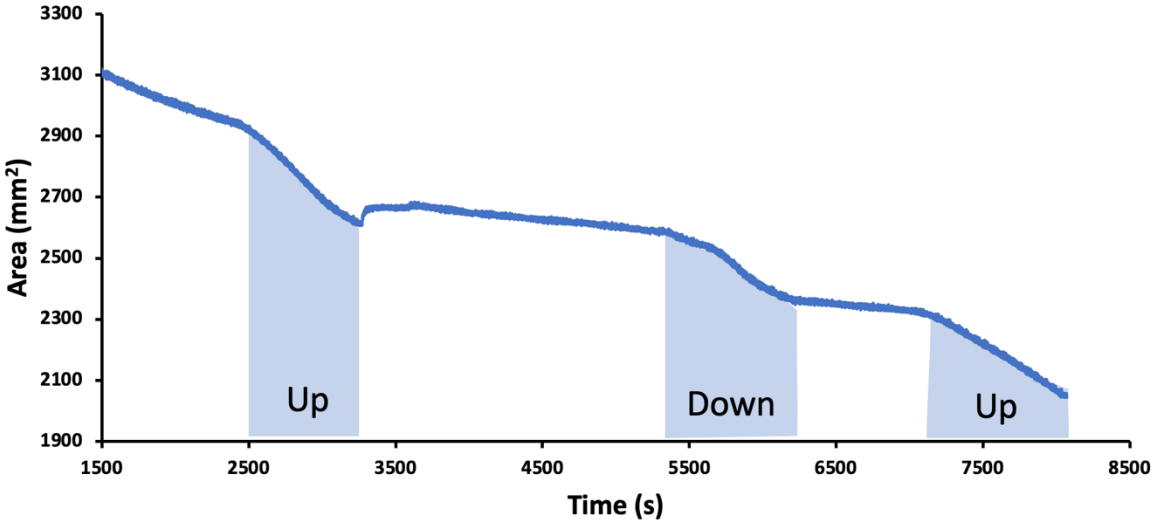


Figure S18 Stability measurements for ligands Hqsal-OR.



Compounds	Up (1)	Down (2)	Up (3)
Compound area (mm^2)	340.37	357.8	193.35
Substrate area (quartz)	340	340	340
Transfer ratio	1.00	1.05	0.57

Figure S19 Langmuir film transfer for $[Fe(qsal\text{-}OC_{12}H_{33})_2]NO_3$ (**1**).



Compounds	Up (1)	Down (2)	Up (3)
Compound area (mm^2)	327.61	249.62	286.06
Substrate area (quartz)	340	340	340
Transfer ratio	0.96	0.73	0.84

Figure S20 Langmuir film transfer for $[Fe(qsal\text{-}OC_{22}H_{33})_2]NO_3$ (**3**).