Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Optoelectronic parameters of peripherally tetra-substituted copper (II) phthalocyanines and photoconductive properties of the fabricated diode for various conditions

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1. Experimental

1.1. Materials and methods

Chloroform ($CHCl_3$), tetrahydrofuran (THF), 4-(trifluoromethoxy)phenol, 4-nitrophthalonitrile and $CuCI_2$ were purchased from Merck and Alfa Aesar and used as received. 4-(4-(trifluoromethoxy) phenoxy) phthalonitrile **(1)** as ligand and its peripheral copper (II) phthalocyanines **(2)** were synthesized according to the literature [1]. All other reagents were obtained from Fluka, Aldrich and Alfa Aesar Chemical Co. and used without further purification. The purity of the products was tested in each step by TLC (SiO_2, $CHCl_3$/MeOH and THF/MeOH). FT-IR spectra were recorded on a Perkin-Elmer spectrum two FT-IR spectrophotometer. Chromatography was performed with silica gel (Merck grade 60) obtained from Aldrich. All reactions were carried out under a dry N_2 atmosphere. Routine UV-vis spectra were obtained using a quartz cuvette on an Agilent Model 8453 diode array spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 300 spectrometer. Mass spectra (MS) were analyzed by MALDI SYNAPT G2-Si Mass Spectrometry. Elemental analysis (C, H and N) was performed using a Thermo Scientific Flash 2000 elemental analyzer.

1.2. Synthesis

1.2.1. 4-(4-(trifluoromethoxy) phenoxy) phthalonitrile (1)

Under an N_2 atmosphere, 4-nitrophthalonitrile (1.00 g, 5.78 mmol) was added dropwise to this mixture at 40 ^{0}C by stirring effectively for 3 days after mixing 4-(trifluoromethoxy)phenol (1.13 g, 6.36 mmol) and finely ground anhydrous K_2CO_3 (~2.30 g, excess) in DMF (10 cm^3). After cooling the reaction mixture to room temperature, it was poured into ca. 150 cm^3 of ice-water media. The obtained product was filtered and then washed with ca. 100 cm^3 of water until the washings became neutral. The obtained product dissolved in $CHCl_3$ and washed with 5% $NaHCO_3$ for removing the unreacted compounds. Then dried over anhydrous Na_2SO_4 and filtered. The product was further purified by silica gel chromatography by using a mixture of $CHCl_3$: MeOH (100/3). Finally, it was crystallized to remove impurities in $CHCl_3$/MeOH(50/10) and isolated by filtration, giving a pure crystallized light blue product.

Yield of **(1)**: 1.52 g (87%); m.p. = 82 °C; Anal. Calcd for $C_{15}H_7F_3N_2O_2$ (304.22 g mol^{-1}) C, 59.22; H, 2.32; N, 9.21; Found: C, 59.21; H, 2.33; N, 9.20. FT-IR (cm^{-1}); 3038 (w, Ar-CH), 2235 (C≡N, st), 1601 (C=C), 1582 (C=N), 1442(st), 1282,1164, 993, 865,735. ^1H NMR ($DMSOd_6$):δ, ppm 8.10 (dd, 1H, ortho to -CN), 7.85 (dd, 1H, ortho to –CN and ortho to -$OArOCF_3$), 7.50-7.39 (m, 3H, meta to -OCF_3 and meta to -CN), 7.35-7.27 (dd, 2H ortho to -OCF_3). ^{13}C-NMR (DMSO-d_6) δ: 161.2, 153.3, 146.0, 137.0, 125.8 *(C-F)*, 124.1, 123.6, 123.0, 122.6, 122.4 *(C-F)*, 119.0 *(C-F)*, 117.4, 116.5, 116.0, 115.6 *(C-F)*, 109.3. MS, m/z: 305.180 $[M+H]^+$.

1.2.2. 2(3), 9(10), 16(17), 23(24)- Tetrakis-(4-(trifluoromethoxy) phenoxy) copper (II) phthalocyanine (2)

In a glass tube, the compound **(1)** (0.10 g, 0.33 mmol) and $CuCl_2$ (0.012 g, 0.1 mmol) were heated in hexanol (1.50 ml) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.05 cm^3) by stirring at 140 ^{0}C under an inert N_2 atmosphere for 6 h. After cooling the obtained greenish-blue product to room temperature, the mixture was diluted with hexane. The crude product was washed several times with first MeOH and CH_3CN for removing impurities. Finally, the product was further purified by silica gel chromatography {$CHCl_3$–THF (10/3 v/v)}. This product is soluble in $CHCl_3$, THF, DMF and DMSO.

Yield of **(2)** 0.045 g (43%), mp > 200 °C. Anal. calcd. for $C_{60}H_{28}CuF_{12}N_8O_8$ (1280.44 g/mol): C, 56.28; H, 2.20; N, 8.75; Found: C, 56.27; H, 2.21; N, 8.76. FT-IR (cm^{-1}); 3070 (w, Ar–CH), 1632(C=C), 1592 (C=N), 1496(st), 1249, 1186, 1014, 832, 735, 607. UV-vis (THF) λ_{max}/nm(Log ε): 673(5.33)(Q_x), 609(4.83) (n-π*), 343(5.26) (B). MS (MALDI-TOF-MS, Dithranol): m/z 1280.059 $[M]^+$.

2. Results and discussion

2.1. Synthesis and characterization

In this study, 4-(4-(trifluoromethoxy) phenoxy) phthalonitrile **(1)** and its peripheral copper (II) phthalocyanines **(2)** were synthesized. For this purpose, the compound **(1)** and anhydrous $CuCl_2$ metal salt were heated in a mixture of 8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.05 cm^3) and hexanol (1.50 cm^3) at ca. 140 °C under an N_2 atmosphere for 6 h **(Scheme S1)**. The structure of the compounds was proved by using a series of spectroscopic techniques such as ^{1}H-NMR, ^{13}C-NMR, FT-IR, mass spectra (MS) and UV-Vis spectroscopic techniques. All the obtained results are consistent with the predicted structures.

The phthalocyanines are characterized by UV-Vis spectroscopy, giving two strong absorption bands called "Q (at roughly 600-700 nm)" band which is a single (narrow) for metallophthalocyanines or split into two Q bands for metal-free phthalocyanines and "B (at roughly 300-350 nm)" band. Compared with the non-peripheral substituted phthalocyanine complexes, peripheral substituted complexes exhibit a blue-shift to about 20 nm in the Q-band region [2]. The absorption spectra of the phthalocyanine **(2)** shows intense Q bands at 673 nm in THF. The B band was observed at 343 nm for **(2)** **(Fig. S1)**.

In the FT-IR spectrum, the vibration at 3218 cm^{-1} for the hydroxyl bond of 4-(trifluoromethylthio)phenol disappeared and this indicated the formation of 4-(4-(trifluoromethoxy) phenoxy) phthalonitrile **(1)**. After the cyclotetramerization reaction, the disappearance of the sharp –C≡N vibration 2235 cm^{-1} of 4-(4-(trifluoromethoxy) phenoxy) phthalonitrile **(1)** proved the formation of the phthalocyanine **(2)** **(Fig. S2)**. The FT-IR spectrum of the phthalocyanine **(2)** is very similar with the exception of small stretching shifts **(Fig. S3)**. The strong –C–F stretching band at 1496 cm^{-1} on the ring of the phthalocyanine **(2)** was observed with a small shift compared to compound **(1)**.

The ^{1}H-NMR and ^{13}C-NMR spectra of 4-(4-(trifluoromethoxy) phenoxy) phthalonitrile **(1)** are very consistent with the expected structure. The carbon signals of the –OCF$_3$ group of the compound **(1)** were observed at 125.8, 122.4, 119.0, 115.6 ppm as a quartet in the DMSO, respectively **(Fig. S4,S5)**.

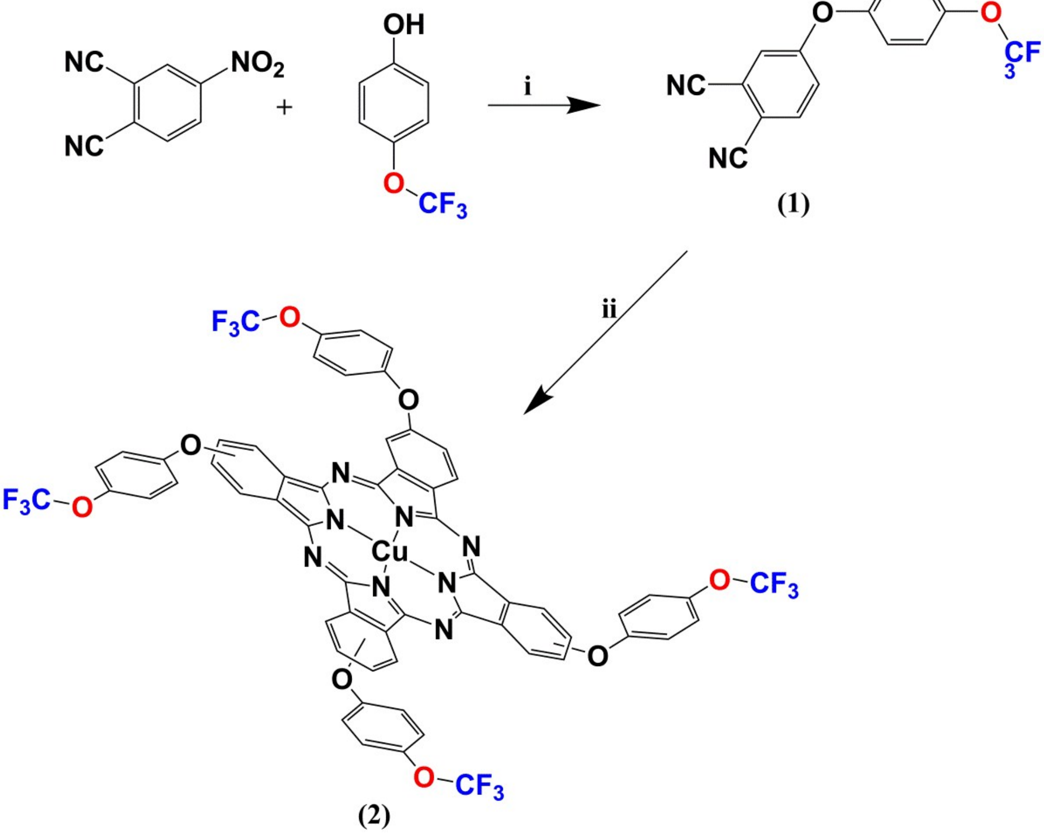
In the mass spectra of the compounds **(1,2)**, the maximum molecular ion peaks were found in accordance with theoretical calculated mass values, where the molecular ion peaks are at m/z m/z: 305.180 [M+H]$^+$ for **(1)** **(Fig. S6)** and m/z 1280.059 [M]$^+$ for **(2)** **(Fig. S7)**, respectively.

2.2. Hirshfeld surface analysis for the compound (1)

The Hirshfeld surfaces, provided by Crystalexplorer program, are the visual results that enable to analyse the inter-molecular interactions. The Hi-resolution Hirshfeld surfaces of compound **(1)** have been presented in **Fig. S8** with the dnorm, curvedness and shape index modes. On the shape index surface, there are three red zones, which are shown by black arrows, that indicate the places of strong D—H···*A* interactions. However, these interaction zones are not seen in the dnorm surface due to the interaction range exceed (or so close to) the Van der Waals ranges. Thus, the PLATON program did not recognize these interactions. Also, the surface of curvedness mode supports the results of shape index due to it has deep points at the same regions.

Figure S9 presents the inter-molecular interactions of C13—H13···*F3* (2.66 Å), C14—H14···*N2* (2.74 Å) and C3—H3···*N1* (2.63 Å) that fits to the red zones shown in **Fig. S8.**

In addition, **Figure S10** presents the percentages of inter-molecular interactions provided by Hirshfeld surface analysis as fingerprint plots (*di:* internal distance, *de*: external distance). The F···H and the N···H bonds have constituted % 19.7 and % 18.8 bonding percentages, respectively. This result strongly supports the presence of D—H···*A* interactions for the F···H and the N···H.



Scheme S1. Synthetic route of the compounds **(1,2)** **i:** K_2CO_3, 4-(trifluoromethoxy)phenol, DMF, 40 °C, 3 days. **ii:** $CuCl_2$, Hexanol, DBU, 140 °C, for 6h.

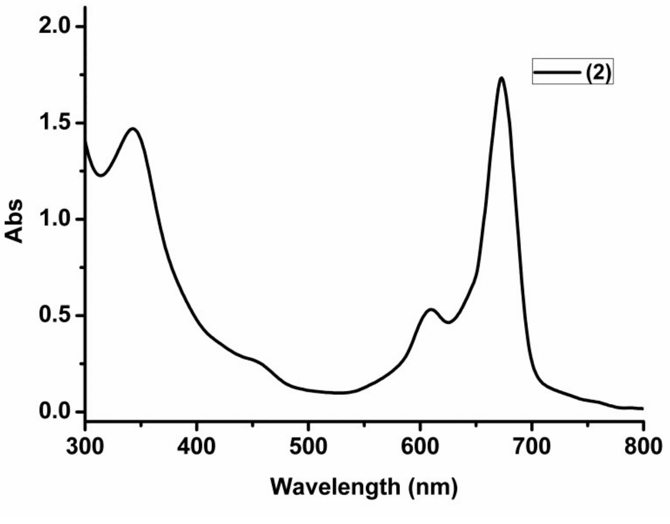


Fig. S1. UV-Vis spectrum of the compound **(2)**

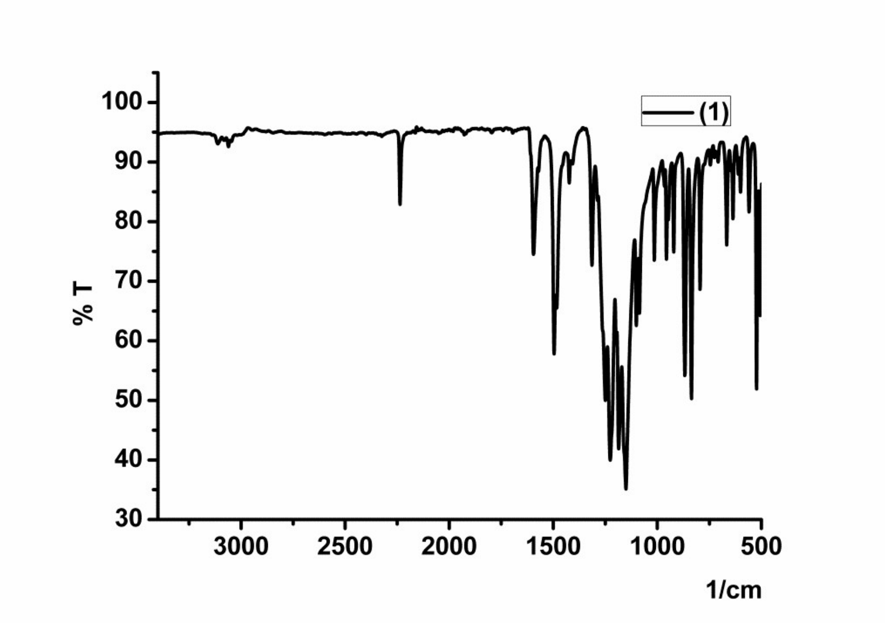


Fig. S2. FT-IR spectrum of the compound **(1)**

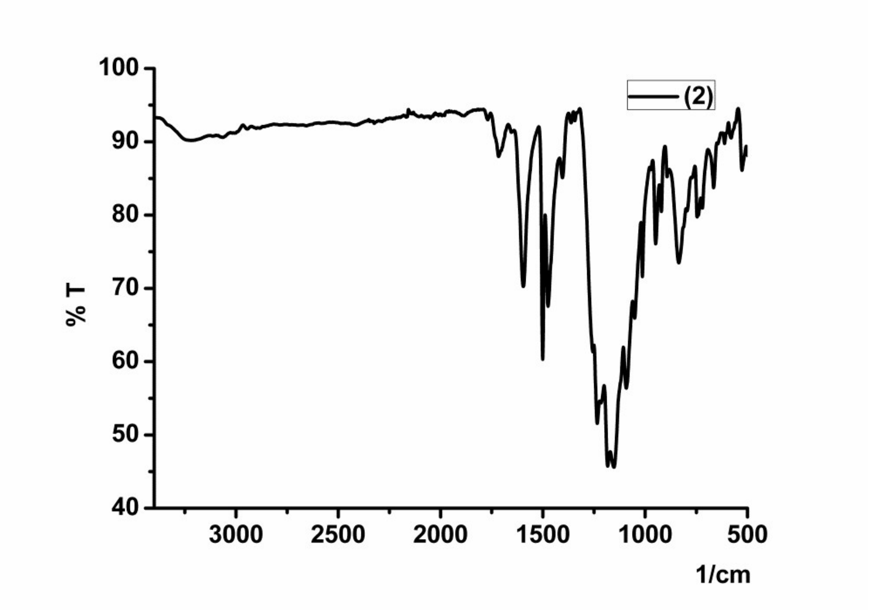


Fig. S3. FT-IR spectrum of the compound **(2)**

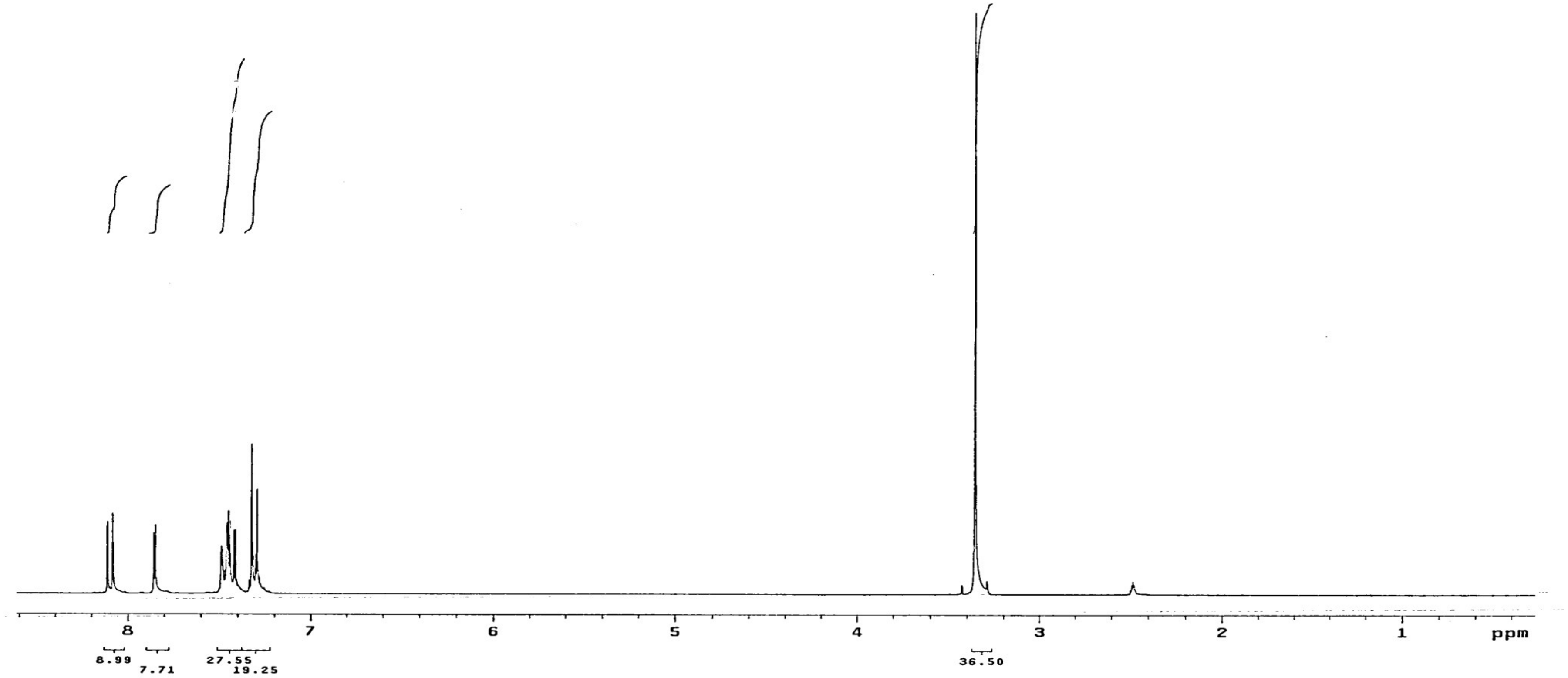


Fig. S4. ^{1}H-NMR spectrum of the compound **(1)**

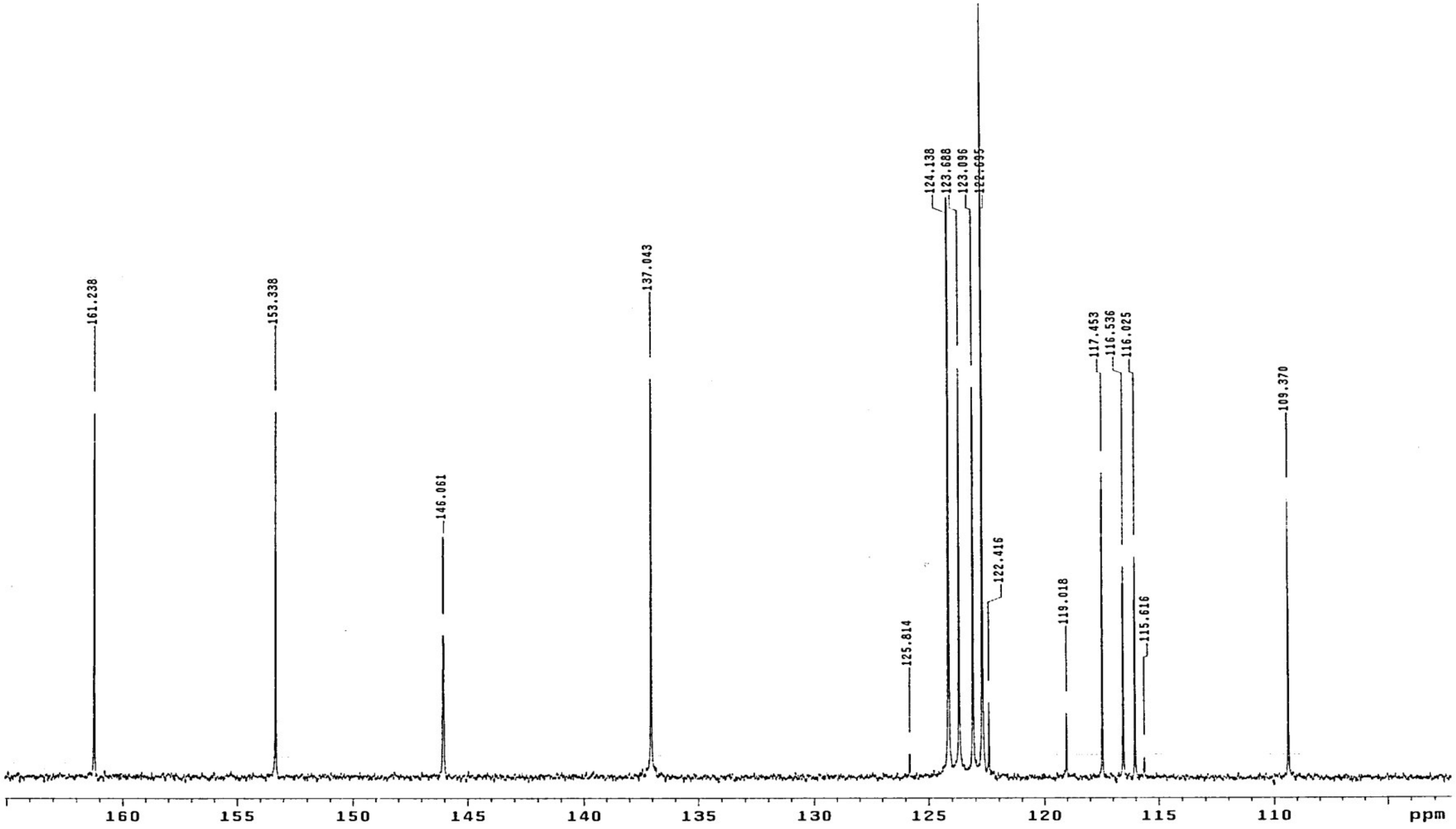


Fig. S5. ^{13}C-NMR spectrum of the compound **(1)**

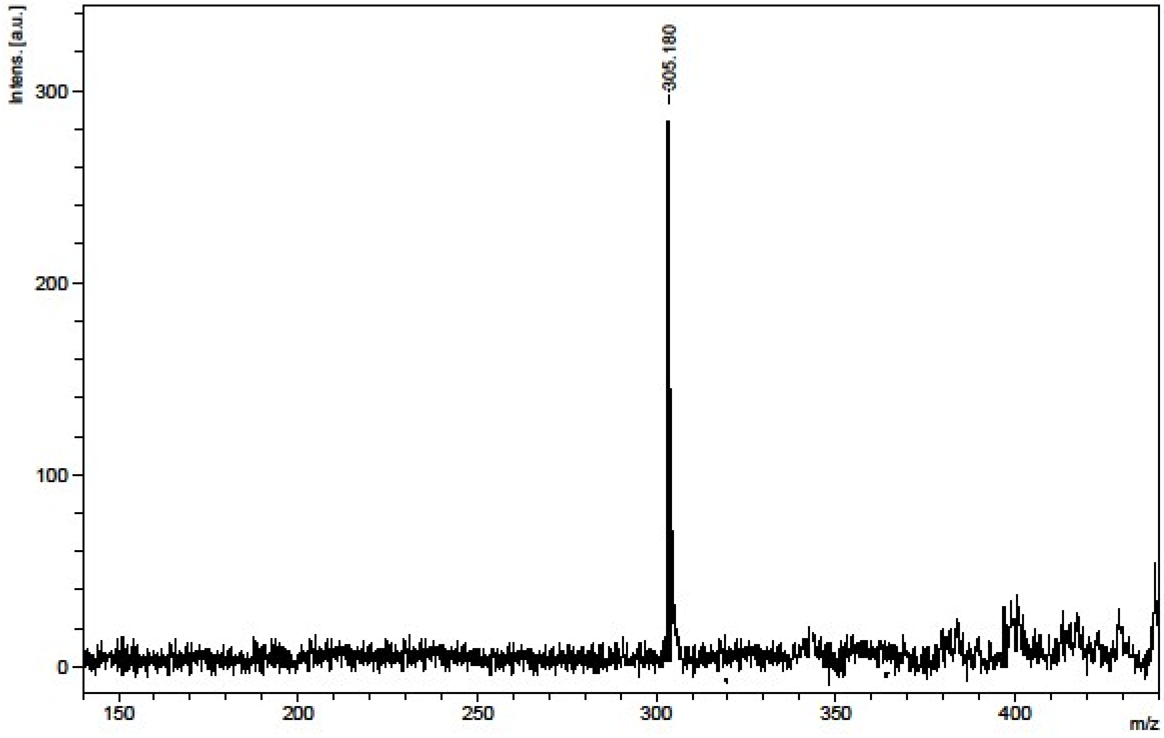


Fig. S6. MALDI-MS spectrum of the compound **(1)**

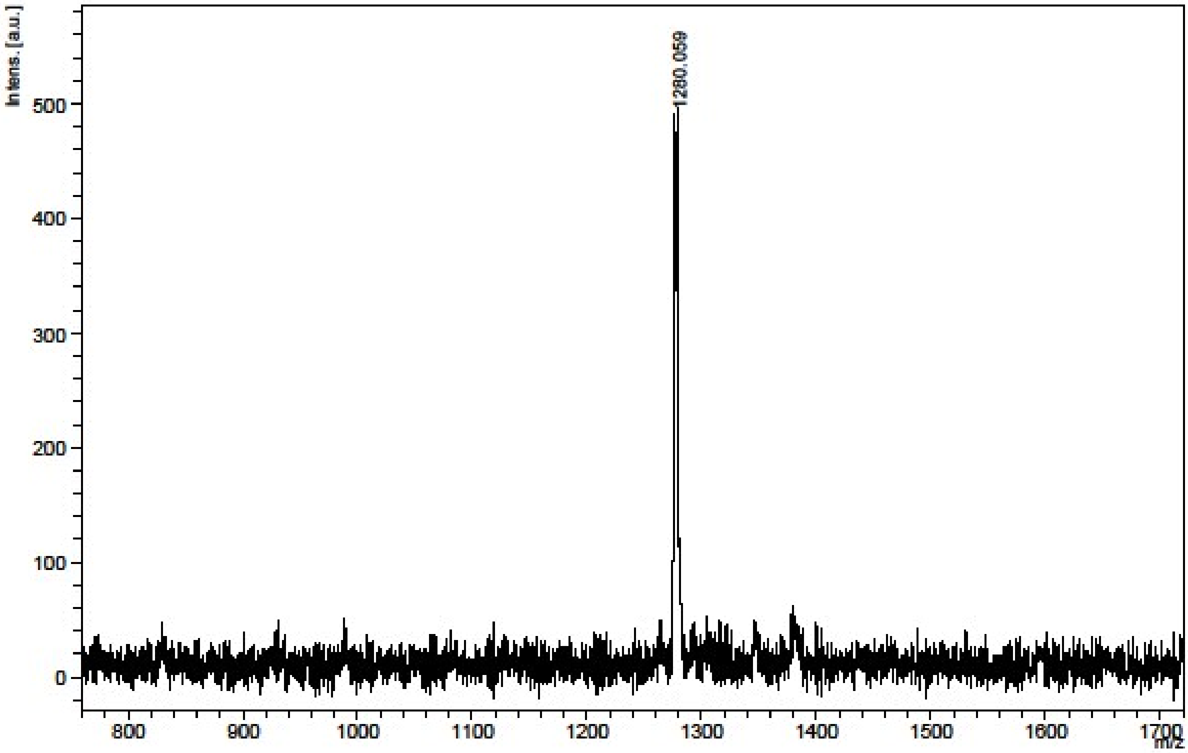
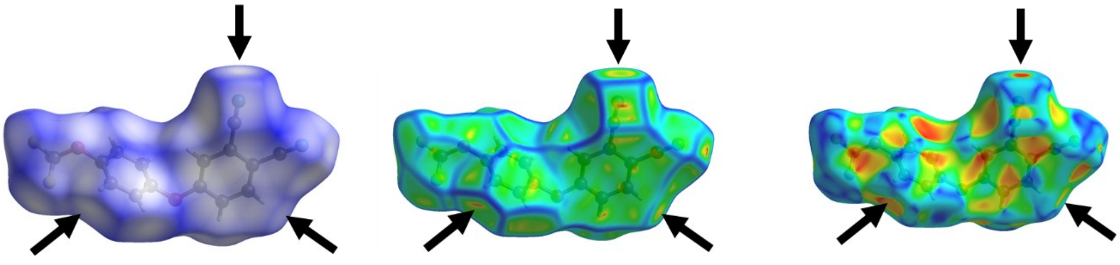


Fig. S7. MALDI-MS spectrum of the compound **(2)**



(a) dnorm

(b)curvedness

(c) shape index

Fig. S8. The Hirshfeld surfaces of compound **(1)** with **(a)** dnorm, **(b)** curvedness and **(c)** shape index modes taken at the same view. The black arrows indicate the red zones that should be strong D—H···*A* interactions.

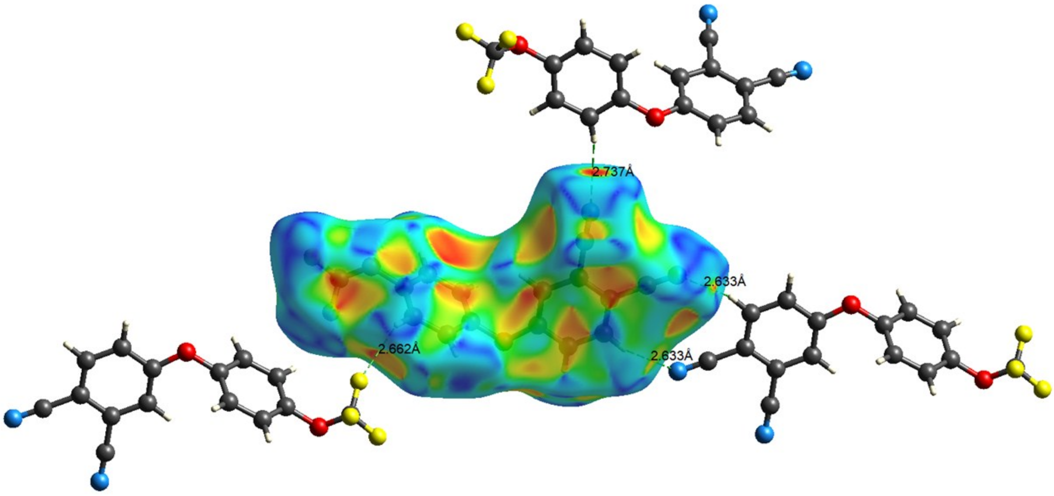


Fig. S9. The C—H···*F* and C—H···*N* interactions that cause the red zones.

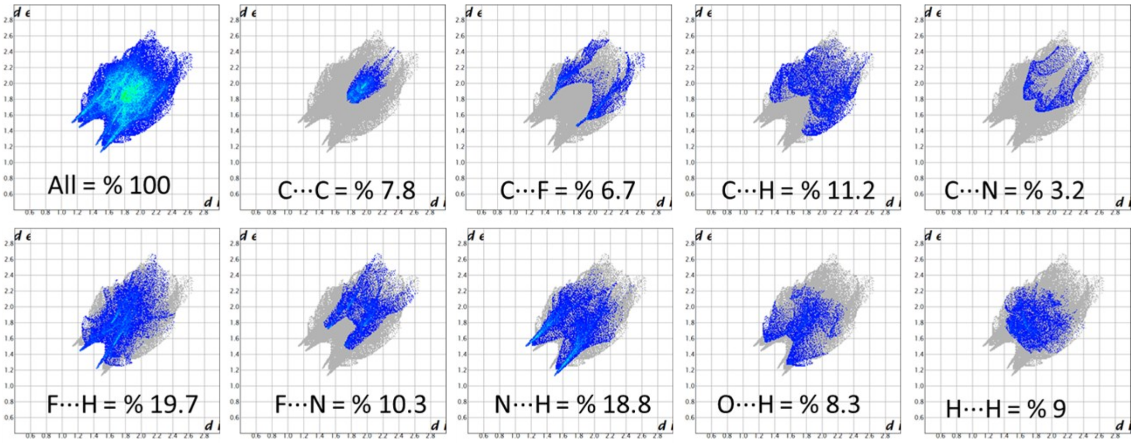


Fig. S10. The interaction percentages of atoms with the nearest neighbor molecules presented as the fingerprint plot for the monoclinic (P 21/c) crystal of compound **(1)**.

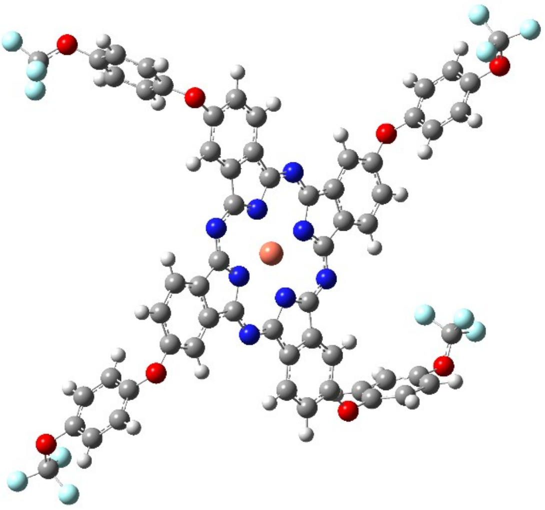


Fig. S11. Optimized structure of compound **(2)**

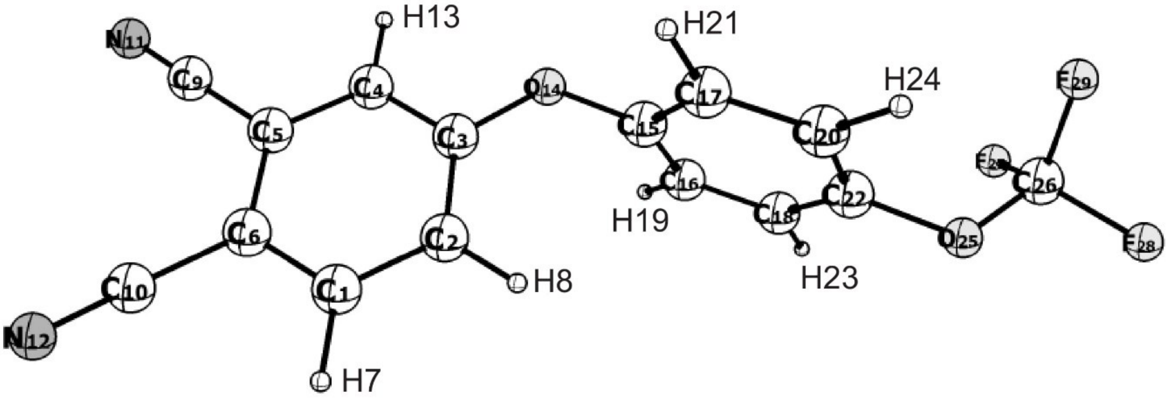


Fig. S12. Atomic labelling of the optimized structure for compound **(1)**

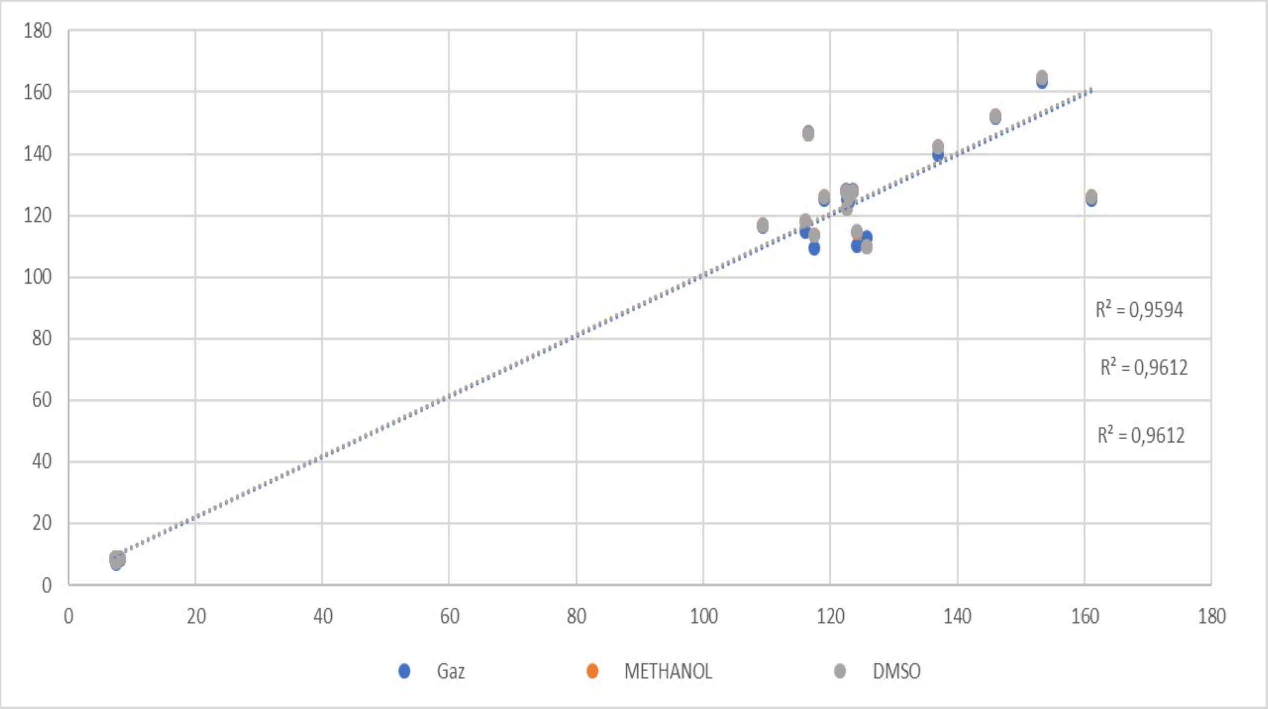


Fig. S13. Graph of experimental values against gas and DMSO phases in theorical calculations for compound **(1)**

Fig. S14. IR spectra of compound **(1)**

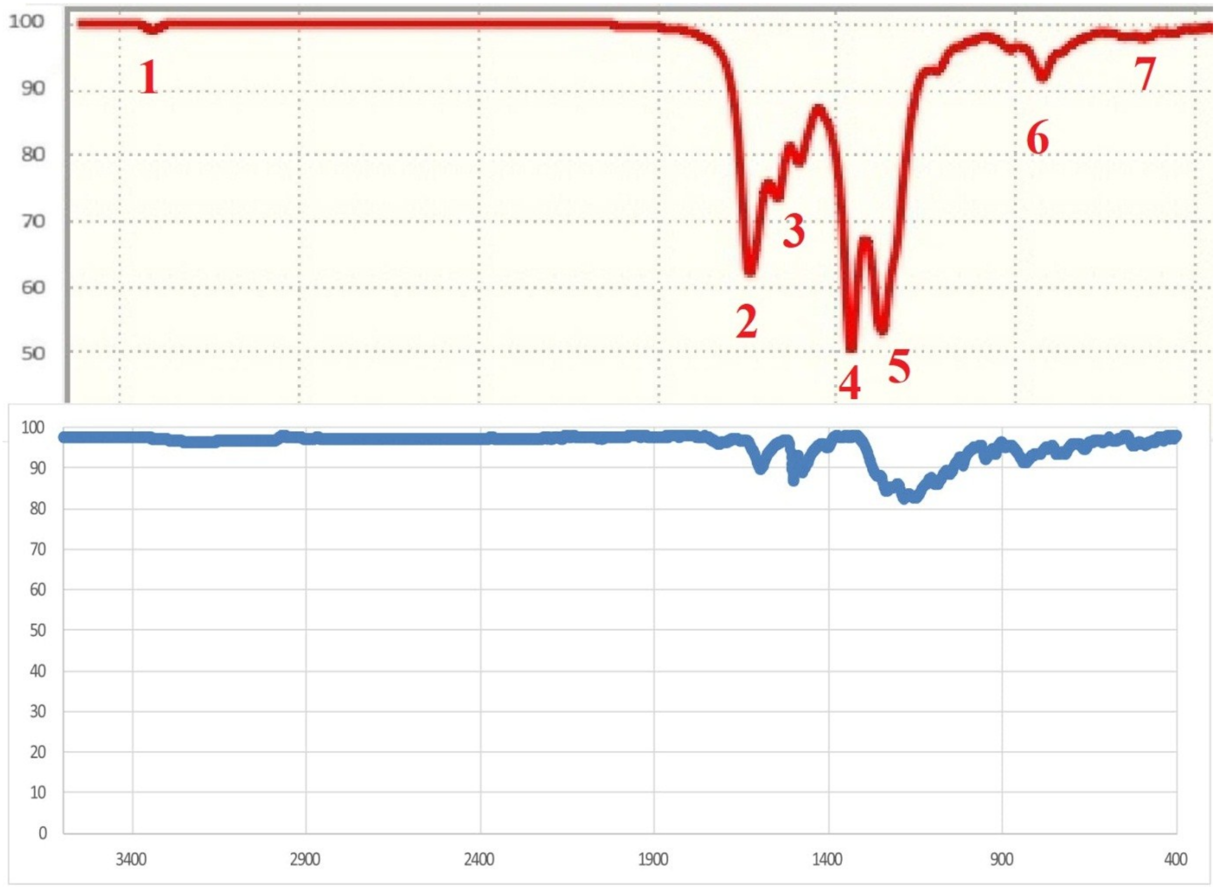


Fig. S15. IR spectra of the obtained compound **(2)**

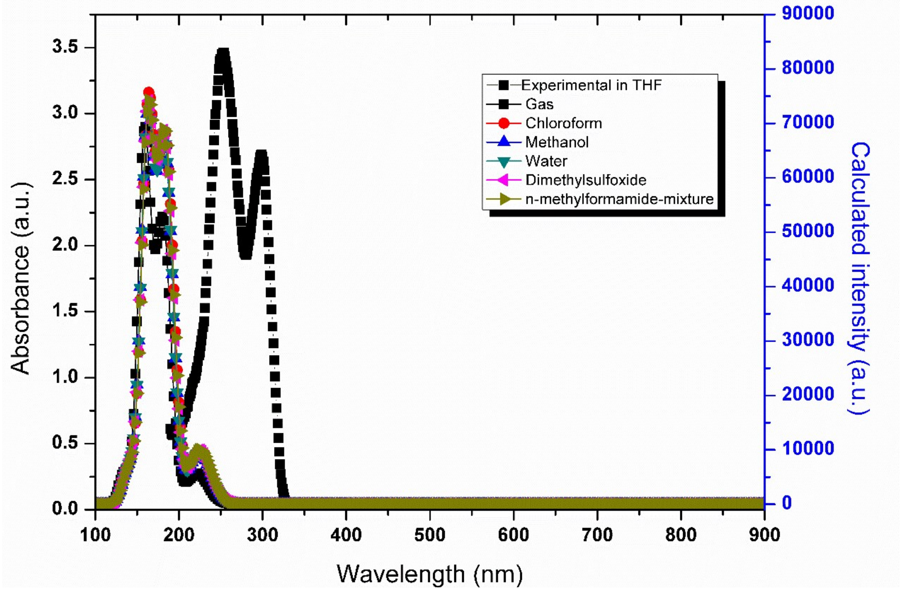
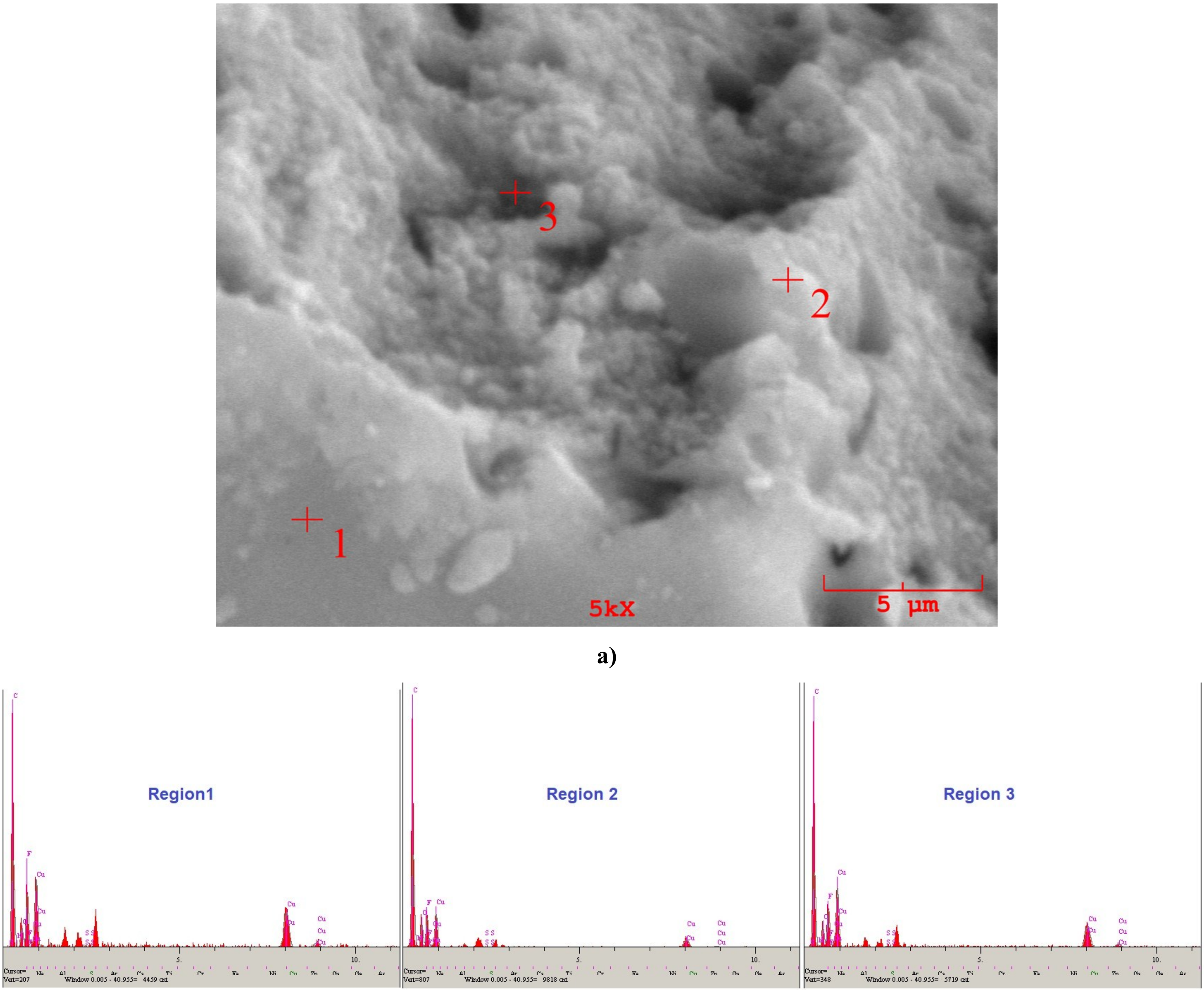


Fig. S16. UV-Vis spectra of ligand compound **(1)**



a)

b)

Fig. S17. The **a)** SEM image of the compound **(2)** and **b)** distributions of the numbers of 1, 2 and 3 based on elements/intensities/concentrations.

Table S1. The calculated quantum chemical parameters with different method (eV)

	E_{HOMO}	E_{LUMO}	I	A	ΔE	H	σ	χ	Pİ	ω	ε	dipol	Energy
B3LYP/3-21g	-7.237	-2.253	7.237	2.253	4.984	2.492	0.401	4.745	-4.745	4.517	0.221	6.829	-30718.876
B3LYP/6-31g	-7.225	-2.481	7.225	2.481	4.744	2.372	0.422	4.853	-4.853	4.964	0.201	6.821	-30879.521
B3LYP/SDD	-7.445	-2.809	7.445	2.809	4.636	2.318	0.431	5.127	-5.127	5.670	0.176	7.280	-30884.341
HF/3-21g	-10.000	1.266	10.000	-1.266	11.266	5.633	0.178	4.367	-4.367	1.693	0.591	7.059	-30549.307
HF/6-31g	-10.054	1.076	10.054	-1.076	11.130	5.565	0.180	4.489	-4.489	1.810	0.552	7.483	-30706.471
HF/SDD	-10.210	0.762	10.210	-0.762	10.973	5.486	0.182	4.724	-4.724	2.034	0.492	7.536	-30710.857
M06-2X/3-21g	-8.752	-1.360	8.752	1.360	7.393	3.696	0.271	5.056	-5.056	3.458	0.289	6.804	-30706.980
M06-2X/6-31g	-8.866	-1.531	8.866	1.531	7.335	3.667	0.273	5.199	-5.199	3.685	0.271	6.908	-30868.252
M06-2X/SDD	-8.851	-1.866	8.851	1.866	6.984	3.492	0.286	5.359	-5.359	4.111	0.243	7.263	-30873.576

Table S2. Energy value of metal atom in lanl2dz basis set

	B3LYP	HF	M062X
Cu^{2+}	-5308.47607	-5282.40567	-5309.81485

Table S3. Energy values of the molecules with different method (eV)

	Compound (2)	**(ΔG)***
B3LYP/3-21g	-128218.4744	-34.4945
B3LYP/6-31g	-128861.3099	-34.7510
B3LYP/SDD	-128881.5140	-35.6735
HF/3-21g	-127509.1661	-29.5335
HF/6-31g	-128139.1271	-30.8393
HF/SDD	-128157.3882	-31.5536
M06-2X/3-21g	-128172.2949	-34.5591
M06-2X/6-31g	-128818.4296	-35.6050
M06-2X/SDD	-128840.2210	-36.1008

*using lanl2dz level for energy value of metal atoms

Table S4. Experimental and calculated ^{1}H-NMR and ^{13}C-NMR chemical shifts (ppm) of compound **(1)**

	GAS	METHANOL	DMSO	EXP.
C1	139.80	142.12	142.15	137.00
C2	114.85	118.07	118.12	116.00
C3	163.52	164.89	164.91	153.30
C4	124.57	126.01	126.03	123.00
C5	125.29	122.35	122.31	122.60
C6	112.76	109.82	109.78	125.80
C9	109.48	113.64	113.70	117.40
C10	110.17	114.60	114.65	124.10
C15	151.83	152.14	152.15	146.00
C16	125.14	126.11	126.13	119.00
C17	125.14	126.12	126.13	161.20
C18	127.94	127.78	127.77	122.40
C20	127.94	127.78	127.77	123.60
C22	147.05	146.64	146.64	116.50
C26	116.61	116.76	116.76	109.30
H7	8.45	8.82	8.83	8.10
H8	7.15	7.56	7.57	7.50
H13	8.46	8.68	8.69	7.85
H19	8.07	8.31	8.31	7.50
H21	8.07	8.31	8.31	7.50
H23	8.43	8.58	8.58	7.35

Table S5. Selected frequencies at HF/6-31G level

Compounds	**Band**	**Frequancy (cm^{-1})**	**Vibration Modes^a**
Compound (1)	1	3395	STRE (aromatic CH)
	2	2557	STRE (N≡C)
	3	1802	STRE (C-C)
	4	1688	BEND (H-C-C)
	5	1465	STRE (C-O)
	6	1377	TORS (H-C=C=C)
	7	1004	TORS (O-C=C=C)
	8	699	STRE (C-F)
Compound (2)	1	3403	STRE (aromatic CH)
	2	1745	STRE (N-C)
	3	1607	BEND (H-C-C)
	4	1458	STRE (C-O)
	5	1367	STRE (C-O)
	6	1207	TORS (H-C=C=C)
	7	914	TORS (O-C=C=C)
	8	332	STRE (Cu-N)
	9	300	BEND (Cu-N-C)

References

[1] N. Farajzadeh, H. Pekbelgin Karaoğlu, M. Akin, N. Saki, M. Burkut Koçak, Synthesis, Photophysical and Biological Properties of New Phthalocyanines Bearing Peripherally 4-(Trifluoromethoxy) phenoxy Groups, Chemistry Select, 4 (2019) 8998-9005.

[2] A. Günsel, M.N. Yarasir, M. Kandaz, A. Koca, Synthesis, H- or J-Type Aggregations, Electrochemistry and In Situ Spectroelectrochemistry of Metal Ion Sensing Lead(II) Phthalocyanines, Polyhedron, 29(18) (2010) 3394-404.