



EDELWEISS PUBLICATIONS  
OPEN ACCESS

<https://doi.org/10.33805/2641-7383.120>  
Volume 3 Issue 1 | PDF 120 | Pages 6

# Edelweiss Chemical Science Journal

Research Article

ISSN: 2641-7383

## Synthesis, Characterization and Self-Assembly Properties of a New Copper-Phthalocyanine Core Acrylate Block Copolymer

Rituparna Saha<sup>1</sup> and Braja K Mandal<sup>2\*</sup>

### Affiliation

<sup>1</sup>Department of Chemistry, Elgin Community College, USA

<sup>2</sup>Department of Chemistry, Illinois Institute of Technology, Chicago, USA

\* **Corresponding author:** Braja K Mandal, Department of Chemistry, Illinois Institute of Technology, 3101 S. Dearborn St., Chicago, IL 60616, USA, E-mail: [mandal@iit.edu](mailto:mandal@iit.edu)

**Citation:** Saha R and Mandal BK. Synthesis, characterization and self-assembly properties of a new copper-phthalocyanine core acrylate block copolymer (2020) Edelweiss Chem Sci J 3: 24-29.

**Received:** Oct 31, 2020

**Accepted:** Dec 11, 2020

**Published:** Dec 17, 2020

**Copyright:** © 2020 Saha R, et al., This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

### Abstract

A new di-block acrylate copolymer with a Copper-Phthalocyanine (CuPc) core has been synthesized via a multi-step reaction scheme involving the atom-transfer radical polymerization. This material displayed amphiphilic character and consists of a CuPc core with eight copolymer arms. This new amphiphilic material and related intermediates have been characterized by UV-Vis, FT-IR, <sup>1</sup>H-NMR and elemental analysis. A preliminary study involving self-assembly properties of this material by optical, atomic force and scanning electron microscopies is presented.

**Keywords:** Copper-phthalocyanine, Amphiphilic materials, Atom-transfer radical polymerization, Aggregates, Self-assembled properties.

**Abbreviations:** CuPc-Copper-Phthalocyanine, Por-Porphyrins, Pc-Phthalocyanines, DMF-Dimethylformamide, DCM-Dichloromethane, FT-IR-Fourier-Transform Infrared Spectroscopy, TLC-Thin Layer Chromatography, tBA-tert-Butyl Acrylate, TEGA-Tri(ethylene glycol) monomethyl ether

### Introduction

In the past decade, the synthesis of functional nano-architectures, aimed at developing electronic and photonic nano-devices to perform specific functions, such as catalysis, chemical sensing, electrical conductivity, photodynamic therapy, etc., has been an intense area of research [1-10]. Most of these activities are driven by the self-assembly and self-organization properties of molecules and require the incorporation of functional building blocks through a well-defined controlled process. Porphyrins (Por), tetraazaporphyrins, Phthalocyanines (Pc) and porphyrazines are examples of tetrapyrrole macrocyclic ring systems, through which mutual non-covalent recognition of specific structural properties, can self-assemble and act as building blocks for self-organized architectures.

Phthalocyanines possess an extended flat hydrophobic aromatic surface and the disc-shaped rigid Pc rings can easily stack through strong intermolecular arene-arene ( $\pi$ - $\pi$ ) interactions, leading to aggregation [11-13]. Other molecular recognition motifs that can self-aggregate are metal-ligand and donor-acceptor interactions and hydrogen bonding [14-16]. Various approaches have been explored in order to control the self-organization of Pc molecules to form well-defined nano-objects. One such approach is the incorporation of these molecules in amphiphilic polymers [17-20].

Pcs have been incorporated in such systems as a side group, as a terminal group, in the main chain and in a polymeric network [21-26]. Kimura et al studied the self-assembly properties of ZnPc-terminated Butyl Acrylate (BA) and Tri(Ethylene Glycol)Methyl Ether Acrylate (TEGA) polymers and have reported formation of nanofibers through self-organization [18]. This group also studied the aggregation

behavior of the amphiphilic block copolymer of poly(norbornene)s containing Pc moieties as a side chain of the polymer backbone that formed spherical micelles in an alkaline aqueous solution [19]. In addition, ordered stacked Pc polymers were prepared in which the Pc moieties were contained in the polymer network and in the main chain of the Pc polymers with reported rod-like nanostructures [20]. Similar polymer systems have also been developed using Por moieties [27-30]. In most cases, the polymerization step has been achieved by controlled/living radical polymerization, such as metathesis polymerization and Atom Transfer Radical Polymerization (ATRP) [18-20, 27-30].

Pcs have mostly been incorporated in amphiphilic polymers as a side group, a terminal group, or in the main chain [31-34]. Although polymer amphiphiles with Por cores have been designed and reported, amphiphilic polymers especially block copolymers with Pc cores; have not been studied well due to synthetic challenges. We report here the synthesis and characterization of a new di-block acrylate copolymer with CuPc core, having a distinct hydrophobic segment composed of tert-Butyl Acrylate (tBA) units, and a hydrophilic segment having Tri(Ethylene Glycol)Monomethyl Ether Acrylate (TEGA) units.

### Experimental

#### Materials and Methods

Unless mentioned otherwise, all reagents were used as received from commercial suppliers without further purification. Dimethylformamide (DMF) used in these reactions was purchased as anhydrous grade

**Citation:** Saha R and Mandal BK. Synthesis, characterization and self-assembly properties of a new copper-phthalocyanine core acrylate block copolymer (2020) Edelweiss Chem Sci J 3: 24-29.



stored in a Sure-Seal™ bottle. Toluene was dried by distillation over freshly cut sodium metal cubes. All reactions involving moisture- and air-sensitive reagents were carried out under an inert atmosphere using high-purity grade argon that was first passed through a column of anhydrous calcium sulfate. Thin Layer Chromatography (TLC) was done on 60, 200  $\mu\text{m}$  thick silica gel flexible plates and 250  $\mu\text{m}$  aluminum oxide flexible plates. Gravity-flow column chromatography was performed on 70-230-mesh, 60Å silica gel or 150-mesh, 58-Å activated neutral aluminum oxide.

Structural characterization by Fourier-Transform Infrared spectroscopy (FT-IR) was carried out using a Thermo Nicolet Nexus 470 FT-IR spectrometer and a Perkin-Elmer System 2000 instrument. The electronic absorption spectra were recorded on a Perkin Elmer (UV/VIS/NIR) spectrometer Lambda-19.  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were recorded by a 300 MHz Bruker instrument. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400 machine. Scanning Electron Microscopy (SEM) was performed by a JEOL JSM5900-LV instrument and Atomic Force Microscopy (AFM) by Picoscan 3000 AFM (Agilent Technology).

### Synthesis of the Phthalocyanine Precursor, 2,3-Dicyano-1,4-bis {2-[2-(2-chloroethoxy)-ethoxy]-ethoxy}benzene (1)

2,3-dicyano-1,4-hydroquinone (11.3958 g, 71.1659 mmol) in 100 mL anhydrous DMF was added to a stirred suspension of  $\text{K}_2\text{CO}_3$  (29.5075 g, 213.5 mmol) and KI (2.9834 g, 18 mmol) in 150 mL anhydrous DMF under inert atmosphere in a 500 mL 3 neck round bottom flask. A solution of 2-[2-(2-chloroethoxy)-ethoxy]ethanol (30 g, 170.7982 mmol) in 10 mL anhydrous DMF was added to it. The reaction mixture was stirred at 70°C for 10 days. It was then cooled to room temperature and filtered under vacuum. The filtrate was poured into a Teflon petridish and DMF was allowed to evaporate. When it was dry, it was kept in the oven at 50°C under vacuum for 2 hours. The brown solid was stirred with water and extracted with chloroform. The organic layer was collected, dried over anhydrous  $\text{MgSO}_4$ , filtered and chloroform was evaporated in a rotary evaporator to give orange colored solid. The solid was purified by column chromatography, using alumina column, eluting with first with Dichloromethane (DCM), followed by 5% methanol in DCM. Evaporation of the solvent yielded compound 1 as white solid Yield: 70%.

FT-IR (KBr):  $\nu=3410, 2908, 2876, 2227, 1493, 1352, 1285, 1195, 1102, 1065, 925, 820, 738, 523, 469 \text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ,  $\delta=2.5$ ):  $\delta=7.62$  (m, 2H),  $\delta=4.56$  (t, 1H),  $\delta=4.28$  (t, 4H),  $\delta=3.77$  (t, 4H),  $\delta=3.59-3.62$  (m, 4H),  $\delta=3.51-3.54$  (m, 4H),  $\delta=3.46$  (t, 4H),  $\delta=3.39-3.42$  (m, 4H).

### Synthesis of Copper Phthalocyanine (CuPc) (2)

1 (2.682 g, 6.32 mmol) and copper powder (0.8 g, 12.59 mmol) were taken in a 10 mL round bottom flask and heated for 5 hours at 170°C under argon. The color of the reaction mixture turned green. The reaction mixture was cooled to room temperature and 10 mL of methanol was added to it. It was stirred overnight and filtered under vacuum. Methanol was evaporated in a rotary evaporator to give green solid. It was purified by column chromatography using alumina. The solvent systems used were DCM, followed by 2-5% methanol in DCM. TLC showed that the product is still not pure. So the fractions that eluted with 2-5% methanol in DCM, were combined and subjected to another column chromatography, with a solvent system of DCM, again followed by 2-5% methanol in DCM. The fractions obtained with the last eluent system were checked with TLC and were found to be pure. Solvent was evaporated to give pure CuPc (2) as a sticky green solid. Yield: 2.2 g, 20%. Anal. Calcd. for  $\text{C}_{83}\text{H}_{123}\text{CuN}_8\text{O}_{32}$  (%): C, 55.1; H, 6.9; N, 6.2. Found (%): C, 54.9; H, 6.8; N, 6.3. FT-IR (KBr):  $\nu=3391, 2901, 2874, 1601, 1505, 1460, 1317, 1268, 1213, 1096, 1068, 924, 890, 808 \text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ,  $\delta=2.5$ ):  $\delta=7.4$  (br,

8H),  $\delta=4.25$  (t, 8H),  $\delta=3.91$  (t, 16H),  $\delta=3.6-3.8$  (m, 80H); UV-Vis ( $\text{DMSO}$ ):  $\lambda_{\text{max}}=741, 662, 325, 269 \text{ nm}$ .

### Synthesis of ATRP macroinitiator (3)

Compound 2 (0.5 g, 0.2765 mmol) was dissolved in 8 mL pyridine in a 25 mL round bottom flask in presence of argon. 2-Bromoisobutryl bromide (7 g, large excess) was dissolved in 5 mL chloroform and added drop wise to a vigorously stirred solution of 11 at 0°C over a period of 1 hour under inert atmosphere. The temperature gradually rose to room temperature and the reaction was allowed to proceed for 24 hours. Chloroform was evaporated in a rotary evaporator. The reaction mixture was then added drop wise to a large excess of water when green solid separated out. It was washed thoroughly with hexane in order to remove unreacted 2-bromoisobutryl bromide. It was then extracted with chloroform and the organic layer was washed thoroughly with water, a saturated solution of  $\text{K}_2\text{CO}_3$  and a saturated solution of NaCl, twice each.

The organic layer was collected, dried over anhydrous  $\text{MgSO}_4$ , and chloroform was evaporated. The green solid was purified by column chromatography using alumina column and chloroform as the eluent. Evaporation of chloroform in a rotary evaporator yielded 12 as a dark green sticky solid. Yield: 0.3 g, 40%. Anal. Calcd. for  $\text{C}_{115}\text{H}_{163}\text{Br}_3\text{CuN}_8\text{O}_{40}$  (%): C, 46; H, 5.5; N, 3.7. Found (%): C, 45.01; H, 5.4; N, 3.6. FT-IR (KBr):  $\nu=2872, 1732, 1599, 1502, 1462, 1388, 1371, 1272, 1211, 1167, 1107, 1073, 928, 875, 756 \text{ cm}^{-1}$ ;  $^1\text{H}$ -NMR (300 MHz,  $\text{DMSO}-d_6$ ,  $\delta=2.5$ ):  $\delta=7.4-7.6$  (m, 8H),  $\delta=4.22$  (t, 16H),  $\delta=3.3-3.76$  (m, 80H),  $\delta=1.86$  (s, 48H);  $\lambda_{\text{max}}=742, 664, 326, 244 \text{ nm}$ .

### Synthesis of the homopolymer, CuPc-core-poly-(tBA) (4a)

The macroinitiator 3 (0.11 g, 0.0367 mmol) was dissolved in dry toluene for 30 minutes under argon atmosphere. N, N, N', N', N''-Pentamethyldiethylenetriamine (PMDETA) (0.063 mL, 0.301 mmol), the monomer t-BA (5 times the weight of the monomer) and  $\text{Cu}(\text{I})\text{Br}$  (0.0432 g, 0.301 mmol) were added sequentially. Three freeze-pump-thaw cycles were performed. The reaction mixture was then heated under vacuum at 90°C for 4 hours under argon atmosphere. Toluene was evaporated. The mixture was washed several times with hexane to remove unreacted PMDETA and the monomer. After each washing, it was centrifuged and hexane was decanted. The green solid was dissolved in chloroform and filtered. The residue is unreacted  $\text{Cu}(\text{I})\text{Br}$ . The filtrate was collected and chloroform evaporated to give green solid.

FT-IR (KBr):  $\nu=2921, 2873, 1732, 1496, 1463, 1388, 1371, 1276, 1168, 1108, 1069, 957, 874, 814, 762, 701, 611 \text{ cm}^{-1}$ ;  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta=7.26$ ):  $\delta=4.22$  (t, 16H),  $\delta=3.6-3.7$  (m, 80H),  $\delta=2.2$  (br, CH of the polymer backbone),  $\delta=1.9$  (br,  $\text{CH}_2$  of the polymer backbone),  $\delta=1.43$  (br,  $(\text{CH}_3)_3\text{C}$  of the t-BA ester group); UV-Vis (DCM):  $\lambda_{\text{max}}=741, 663, 325, 231 \text{ nm}$ .

### Synthesis of the block copolymer, CuPc-core- poly-(tBA)-co-poly-(TEGA) (4b)

4b was made following the same procedure as the synthesis of 4a. In this case, 4a itself was used as the macroinitiator for the polymerization reaction.

$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta=7.26$ ):  $\delta=7.6$  (m, 8H),  $\delta=4.3$  (t, 16H,  $\text{CH}_2\text{OCO}$ ),  $\delta=3.5-3.75$  (m,  $\text{OCH}_2$ ),  $\delta=3.38$  (s,  $\text{CH}_3$  of the TEGacrylate group),  $\delta=2.2-2.5$  (br, m, protons in polymer backbone),  $\delta=1.44$  (s,  $(\text{CH}_3)_3\text{C}$  of the t-BA ester group); UV-Vis (DCM):  $\lambda_{\text{max}}=737, 292 \text{ nm}$ .

### Synthesis of TEGA monomer (5)

Tri(ethylene glycol) monomethyl ether (1.5 g, 9.1352 mmol) was dissolved in 5 mL anhydrous THF. Acryloyl chloride (1.5 g, 16.5727 mmol) and triethyl amine (3.18 mL, 22.838 mmol) were added to it. The reaction mixture was stirred under argon atmosphere overnight at

room temperature. It was then poured into water and extracted with chloroform. The organic layer was washed several times with a saturated solution of  $\text{Na}_2\text{CO}_3$  and a saturated solution of  $\text{NaCl}$ . It was dried over anhydrous  $\text{MgSO}_4$ , filtered and chloroform was evaporated from the filtrate to yield the TEGA monomer (5) as colorless liquid. 5 were purified by column chromatography using alumina. 2% methanol in chloroform was used to elute the pure fraction.

FT-IR (KBr): 2872, 1722, 1631, 1455, 1411, 1269, 1195, 1113, 987, 853,  $806\text{ cm}^{-1}$ ;  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$   $\delta=7.26$ ):  $\delta=6.35$  (dd, 1H),  $\delta=6.1$  (dd, 1H),  $\delta=5.79$  (dd, 1H),  $\delta=4.25$  (t, 2H),  $\delta=3.46$ -3.7 (m, 10H),  $\delta=3.33$  (s, 3H).

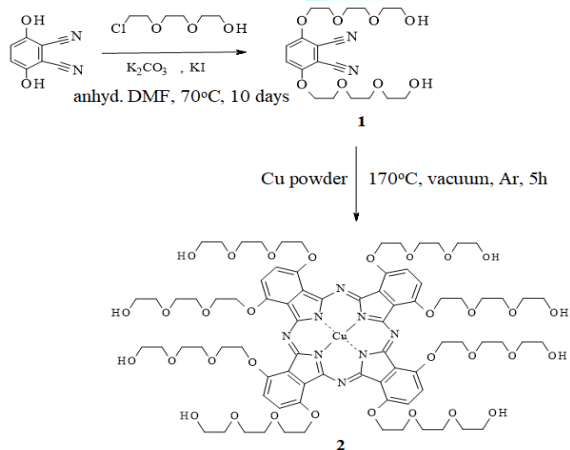
## Results and Discussion

### Retro-synthetic Analysis

The two key components of the retro-synthetic design for this project are (i) an appropriate core molecule functionalized with initiator groups and (ii) polymerization to form the arms. Therefore, in order to make CuPc core functionalized polymer arms (4a and 4b), a CuPc derivative containing eight bromoisobutyryl initiator moieties (3) must be synthesized first. This macro-initiator could be made from a CuPc-centered tri(ethyleneoxy) intermediate (2), a CuPc derivative with peripherally substituted hydroxyl (-OH) functional groups. That leaves 2 was to be constructed by cyclo-tetramerization of a phthalonitrile precursor (1).

### Synthesis and Characterization

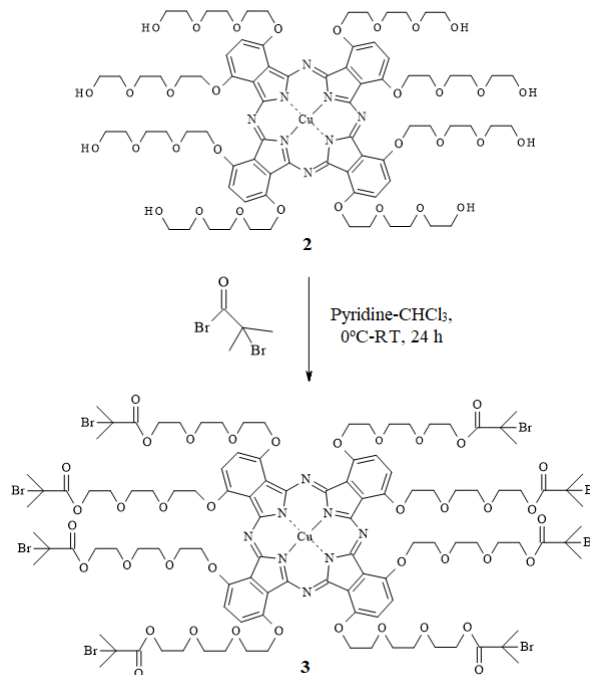
Phthalonitriles are the most commonly used precursors for the synthesis of phthalocyanine derivatives. A disubstituted phthalonitrile derivative (1) was synthesized as the precursor of 2 by an O-alkylation reaction in which 2,3-dicyanohydroquinone was alkylated by treatment with 2-[2-(2-chloroethoxy)-ethoxy]ethanol in the presence of anhydrous potassium carbonate and a catalytic amount of potassium iodide (Scheme 1). The reaction was carried out in anhydrous DMF. The same reaction conditions were followed as reported by Xue et al., [16]. After evaporation of DMF, the crude product was extracted with chloroform and purified by column chromatography to afford pure 1 as a white solid.



**Scheme 1:** Synthesis of CuPc precursor (1) and CuPc (2).

The first attempt to synthesize CuPc was by refluxing 1 in 2-(dimethylamino)ethanol in the presence of copper acetate under an argon atmosphere, but no characteristic green color of Pc was obtained, even after 3 days. Next, we tried to synthesize the CuPc via its  $\text{Li}_2\text{Pc}$  [35]. After purification, the desired CuPc was obtained, but in very low

yield (12%). The next attempt was via the isoindoline route where 1 was first converted into its isoindolene by treating with ammonia in the presence of sodium methoxide in methanol, followed by self-condensation of the isoindolene into CuPc, in the presence of copper acetate, but without success. Another attempted route to 2 was by reacting 1 with copper acetate in dry quinoline at  $220^\circ\text{C}$  for 3 hours, but the characteristic green color of Pc was not observed. Finally, we succeeded in synthesizing 2 from 1 by a solvent-free method [36]. The phthalonitrile derivative was stirred with Cu powder at a very high temperature [36]. The optimum temperature for our system was found to be  $170^\circ\text{C}$  under vacuum for 5 hours (Scheme 1). Unreacted Cu powder was filtered off and pure 2 were obtained as a sticky green solid after column chromatography. The macroinitiator 3, with bromoisobutyryl initiating sites, was synthesized by acylation of the peripheral hydroxyl groups in 1 with a large excess of 2-bromoisobutyryl bromide. The reaction was carried out in a mixture of chloroform and pyridine and the temperature was allowed to rise from  $0^\circ\text{C}$  to room temperature and maintained there for 24 hours (Scheme 2). The crude product was extracted with chloroform and washed thoroughly with saturated solutions of Potassium Carbonate ( $\text{K}_2\text{CO}_3$ ) and Sodium Chloride ( $\text{NaCl}$ ). Pure 3 was obtained as a bright green solid after column chromatography.



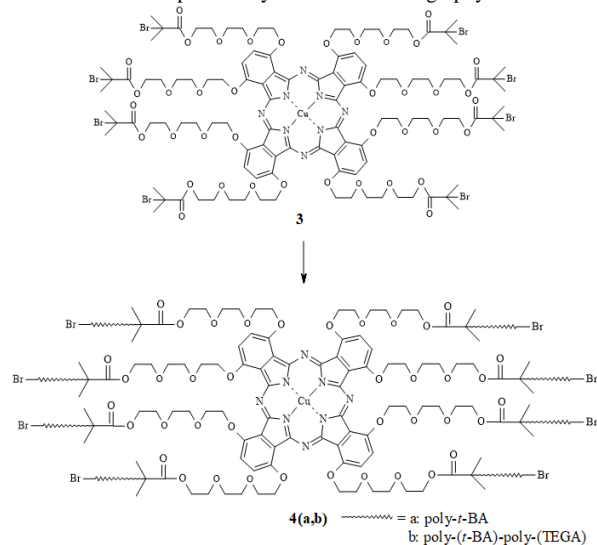
**Scheme 2:** Synthesis of CuPc macroinitiator (3).

The polymerization reactions were performed under ATRP conditions (Scheme-3). Two monomers were chosen: (i) tert-Butylacrylate (t-BA) and (ii) Tri(ethylene glycol)Monomethyl Ether Acrylate (TEGA). While the polymer chain composed of t-BA units imparts hydrophobicity to the system, the one composed of TEGA monomers provides hydrophilicity. Accordingly, the CuPc-core block copolymer poly-(t-BA)-poly-(TEGA) will be amphiphilic in nature. The monomer TEGA (5) was obtained from tri(ethylene glycol)monomethyl ether and acryloyl chloride following the conditions previously reported for the preparation of acrylated PEG derivatives [37]. Copper (I) Bromide  $[\text{Cu(I)Br}]$  was used as catalyst and  $\text{N,N,N',N',N''}$ -Pentamethyldiethylenetriamine (PMDETA) as the ligand. In a typical polymerization procedure, the Pc-core macroinitiator: CuBr: ligand ratio was 1: 8.2: 8.2 and the amount of monomer added was 5 times the weight of the initiator. Polymerization reactions were carried out in

**Citation:** Saha R and Mandal BK. Synthesis, characterization and self-assembly properties of a new copper-phthalocyanine core acrylate block copolymer (2020) Edelweiss Chem Sci J 3: 24-29.



solution with toluene as solvent under argon atmosphere. The purification procedure was modified, by first extracting with chloroform and then purified by column chromatography.



**Scheme 3:** Polymerization of t-BA and TEGA by ATRP.

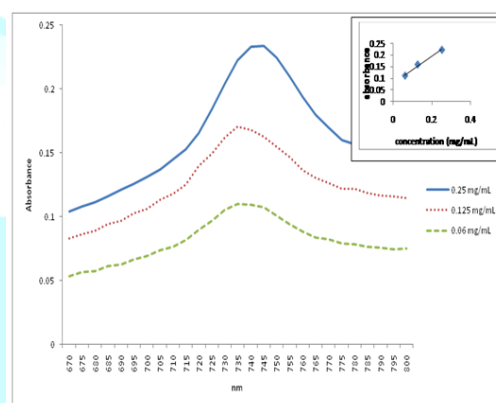
The FT-IR spectrum of the phthalonitrile precursor (**1**) showed strong O-H stretching at  $3410\text{ cm}^{-1}$  and aromatic C-H stretch at  $3092\text{ cm}^{-1}$ . Bands at  $2907\text{ cm}^{-1}$  and  $2876\text{ cm}^{-1}$  are indicative of  $\text{CH}_2$  asymmetric and  $\text{CH}_2$  symmetric stretching frequencies. The strong peak at  $2228\text{ cm}^{-1}$  is typical of  $\text{C}\equiv\text{N}$  stretching in aromatic nitriles. The presence of both aromatic and aliphatic C-H vibrations proves that the O-alkylation step was successful. The  $\text{C}\equiv\text{N}$  peak at  $2228\text{ cm}^{-1}$  was completely disappeared in the spectrum of CuPc (**2**), indicating complete cyclotetramerization of **1**. The strong peak at  $3390\text{ cm}^{-1}$  is due to O-H stretching. The aromatic C-H stretching vibration is seen at  $3080\text{ cm}^{-1}$  and the positions of symmetric and asymmetric aliphatic C-H stretching vibrations remain the same as those for compound **1**. In the FTIR spectrum of the macroinitiator **3**, successful acylation with 2-bromoisobutyl bromide is evident from the disappearance of the O-H and the formation of the ester linkage comes from the strong ester carbonyl peak at  $1732\text{ cm}^{-1}$ . The FT-IR spectrum of the homopolymer, **4a**, had characteristic peaks similar to those of **3**, with the common features being (i) absence of O-H, (ii) presence of  $\text{CH}_2$  asymmetric and  $\text{CH}_2$  symmetric frequencies, and (iii)  $>\text{C}=\text{O}$  around  $1730\text{ cm}^{-1}$ . Formation of TEGA was also confirmed by FT-IR from the aliphatic  $\text{CH}_2$  peaks around  $2900\text{ cm}^{-1}$  and the ester carbonyl peak at  $1722\text{ cm}^{-1}$ .

$^1\text{H-NMR}$  of the phthalonitrile precursor **1** in  $\text{DMSO-d}_6$  shows chemical shifts for the aromatic protons at  $\delta=7.62(\text{m})$ , for the OH protons at  $\delta=4.56(\text{t})$ , for the  $\text{ArOCH}_2$  protons at  $\delta=4.28$  as a triplet and for all the other  $\text{CH}_2\text{O}$  protons at  $\delta=3.39\text{--}3.77$  as multiplet. The chemical shifts for these protons remain almost the same in the CuPc (**2**), with the aromatic protons at  $\delta=7.4$ , OH protons at  $\delta=4.25$ ,  $\text{ArOCH}_2$  protons at  $\delta=3.91$  and  $\text{CH}_2\text{O}$  protons at  $\delta=3.6\text{--}3.8$ . In the  $^1\text{H-NMR}$  spectrum of the macroinitiator **3**, the presence of a singlet at  $\delta=1.86$ , due to the chemical shift of the protons in the  $\text{CH}_3$  groups at the end of the side chains, proves that the esterification step has been successful.

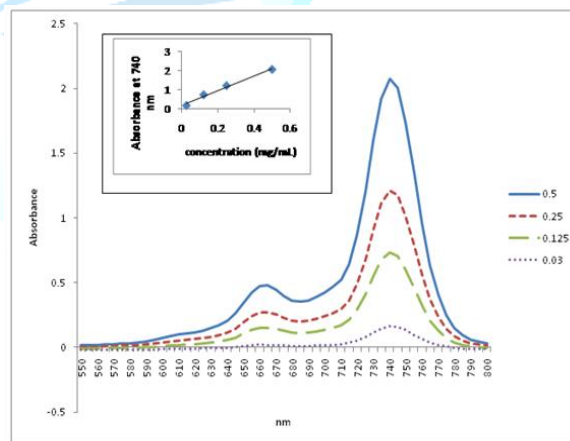
The peaks for the  $\text{ArOCH}_2$  protons are at  $\delta=4.22$  and for the  $\text{CH}_2\text{OCO}$  protons at  $\delta=3.75$ . Besides the aromatic protons and the  $\text{ArOCH}_2$  protons at  $\delta=7.26$  and  $\delta=4.22$ , respectively, the  $^1\text{H NMR}$  spectrum of the poly-t-BA (**4a**) exhibits peaks at  $\delta=2.2$  for CH protons of the polymer backbone, at  $\delta=1.9$  for the  $\text{CH}_2$  of the polymer backbone and at  $\delta=1.43$  ( $\text{CH}_3$ )<sub>3</sub>C protons of the t-BA ester group. The success of the copolymerization reactions to synthesize **4b** is conspicuous from its  $^1\text{H}$

NMR spectra. It shows peaks attributed to the tert-butyl resonance ( $\delta=1.44$ ) as well as the to the  $\text{OCH}_3$  resonance ( $\delta=3.38$ , singlet). The  $^1\text{H-NMR}$  spectrum of TEGA monomer (**5**) shows three doublets of doublet for the three protons in the  $\text{C}=\text{C}$  at  $\delta=6.35$ ,  $\delta=6.1$  and  $\delta=5.79$  and the  $\text{OCH}_3$  resonance at  $\delta=3.33$ .

The UV-Vis spectroscopy of compounds **2-4** was performed in DCM. All exhibit the characteristic Q band of Pc molecules. Further study was carried out with the homopolymer (**4a**) and the copolymer (**4b**) in order to investigate their aggregation properties at low concentrations. This was done by studying their UV-Vis absorption behavior at different concentrations and plotting the intensity of their Q-bands at different concentrations against the sample concentration at selected absorption wavelength (corresponding to the wavelength of the Q bands). The linear relationship between concentration and absorbance, as displayed in **Figure 1** and **Figure 2**, strictly follows the Lambert-Beer Law, suggesting that neither of them form aggregates at low concentrations.



**Figure 1:** Plot of UV-Vis Absorption Spectra of Poly-t-BA (**4a**) at Different Concentrations against Wavelength in DCM. Inset: Plot of the Q Band Absorbance versus Concentration at 735 nm.



**Figure 2:** Plot of UV-Vis Absorption Spectra of Poly-t-BA-poly-TEGA (**4b**) at Different Concentrations against Wavelength in DCM. Inset: Plot of the Q Band Absorbance versus Concentration at 735 nm.

The solubility properties of compounds (**1-4**), summarized in **Table 1**, indicating that the copolymers are soluble in polar solvents.

### Study of Self-Assembly Properties

A preliminary study was carried out to investigate the self-assembly properties of the CuPc-core block copolymer poly-(t-BA)-poly-



(TEGA) (4b), using optical microscopy, AFM and SEM. The copolymer was dissolved in methanol (10 mg per mL). A drop of it

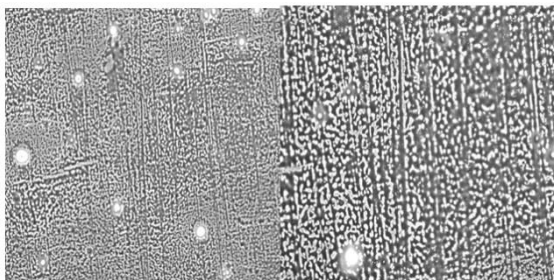
was placed on the substrate and the solvent was allowed to evaporate completely.

Compound	Diethyl ether	THF	Hexane	Acetone	Ethyl acetate	CH <sub>3</sub> CN	DCM	MeOH
1	--	--	--	--	+	++	++	++
2	--	--	--	--	--	+	++	++
3	--	--	--	--	--	+	++	++
4 (a, b)	--	++	--	+	--	+	+	+

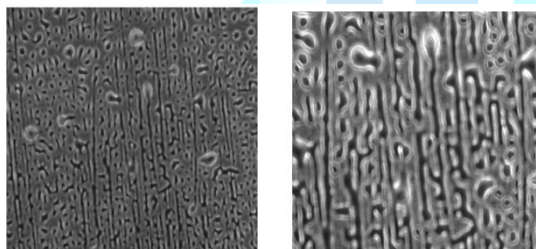
Note: +: Soluble on warming, ++: Highly Soluble, --: Insoluble

**Table 1:** Solubility Characteristics of Compounds 1-4.

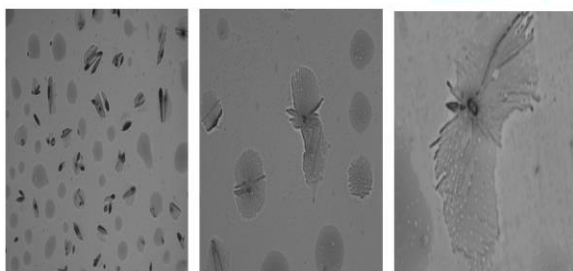
**Figures 3-5** show images from an optical microscope at 10x, 20x and 40x magnifications, on days 1, 3 and 7. A glass was used as the substrate. The images of days 1 and 3 show that the polymer is in the process of self-assembling (**Figure 3** and **Figure 4**). By the day 7, this process was complete and fibrous assemblies can be observed (**Figure 5**).



**Figure 3:** Optical Microscope Image of **4b** on Day 1: (a) 10x (b) 20x.



**Figure 4:** Optical Microscope Image of **4b** on Day 3: (a) 10x (b) 20x.

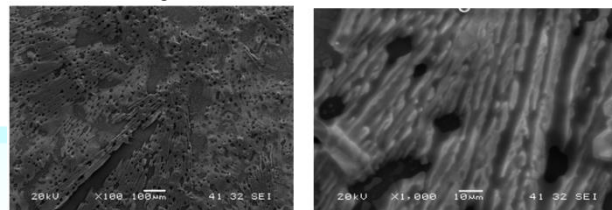


**Figure 5:** Optical Microscope Image of **4b** on Day 7: (a) 10x (b) 20x (c) 40x.

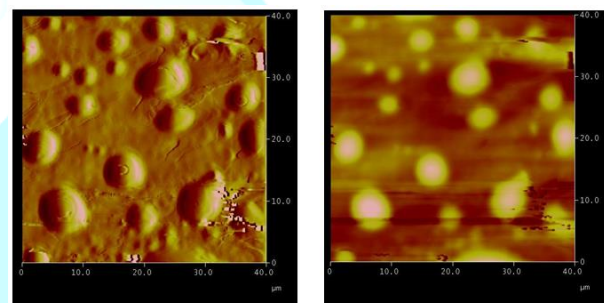
The substrate used for SEM study was silicon wafer. The sample studied was day 7 after evaporation of the solvent. Again, self-assembled fibrous structures, with fiber width of ~2 micron, were observed (**Figure 6**). Tapping mode AFM of the sample on Highly Ordered Pyrolytic Graphite (HOPG) on day 7 showed spherical assemblies with diameters 2.5-3.8  $\mu\text{m}$ . (**Figure 7**).

In conclusion, we believe that since the copolymer has a hydrophilic segment at the peripheral sites, it forms spherical assemblies on

hydrophobic substrate HOPG, whereas on hydrophilic substrates, e. g., silicon wafer and glass, it forms fibrous assemblies.



**Figure 6:** SEM of **4b** on Day 7 (Substrate: Silicon Wafer).



**Figure 7:** AFM of **4b** on Day 7 (Substrate: HOPG).

## References

- Li Y, Wong RCH, Yan X, Dennis KP and Pui-Chi L. Self-assembled nanophotosensitizing systems with zinc(ii) phthalocyanine-peptide conjugates as building blocks for targeted chemo-photodynamic therapy (2020) ACS Appl Bio Mater 3: 5463-5473. <https://doi.org/10.1021/acsabm.0c00214.s001>
- Demazeau M, Gibot L, Mingotaud AF, Vicendo P, Roux C, et al. Rational design of block copolymer self-assemblies in photodynamic therapy (2020) Beilstein J Nanotechnol 11: 180-212. <https://doi.org/10.3762/bjnano.11.15>
- Shokurov AV, Yagodin AV, Martynov AG, Gorbunova YG and Selektor SL. Phthalocyanine monolayers self-assembled directly from its thiobenzoyl derivative (2020) ECS J Solid State Sci Technol 9: 051006. <https://doi.org/10.1149/2162-8777/ab9a5e>
- Feng X, Liu C, Wang X, Jiang Y, Yang G, et al. Functional supramolecular gels based on the hierarchical assembly of porphyrins and phthalocyanines (2019) Front Chem 7. <https://doi.org/10.3389/fchem.2019.00336>
- Pan L, Jia K, Huang Y and Liu X. Formation of organometallic microstructures via self-assembling of carboxylated zinc phthalocyanines with selective adsorption and visible light-driven photodegradation of cationic dyes (2017) J Mater Sci 53: 492-505. <https://doi.org/10.1007/s10853-017-1531-6>
- Aimi J, Komura M, Iyoda T, Saeki A, Seki S, et al. Synthesis and self-assembly of phthalocyanine-tethered block copolymers (2015) J Mater Chem C 3: 2484-2490. <https://doi.org/10.1039/c4tc02778g>

**Citation:** Saha R and Mandal BK. Synthesis, characterization and self-assembly properties of a new copper-phthalocyanine core acrylate block copolymer (2020) Edelweiss Chem Sci J 3: 24-29.



7. Yan D, Feng Y and Wang C. Self-assembled array of rectangular single-crystal microtubes of perchlorinated copper phthalocyanines (2013) *Prog Nat Sci Mater Int* 23: 543-548. <https://doi.org/10.1016/j.pnsc.2013.11.008>
8. Wang Y, Xu H, Wang H, Li S, Gan W, et al. Temperature dependent 2D self-assembled motif transition of copper-phthalocyanine derivatives at air/HOPG interface: an STM study (2014) *RSC Adv* 4: 20256-20261. <https://doi.org/10.1039/c3ra46651e>
9. Zhao Y, Ding J and Huang XB. Synthesis and self-assembly of phthalocyanines bearing sulfur-containing substituents (2014) *Chinese Chem Lett* 25: 46-50. <https://doi.org/10.1016/j.ccllet.2013.10.034>
10. Imahori H, Uneyama T, Kurotobi K and Takano Y. Self-assembling porphyrins and phthalocyanines for photoinduced charge separation and charge transport (2012) *Chem Commun* 48: 4032. <https://doi.org/10.1039/c2cc30621b>
11. Bayda M, Dumoulin F, Hug GL, Koput J, Gorniak R, et al. Fluorescent H-aggregates of an asymmetrically substituted mono-amino Zn (ii) phthalocyanine (2017) *Dalt Trans* 46: 1914-1926. <https://doi.org/10.1039/c6dt02651f>
12. Jeong J, Kumar RS, Mergu N and Son YA. Photophysical, electrochemical, thermal and aggregation properties of new metal phthalocyanines (2017) *J Mol Struct* 1147: 469-479. <https://doi.org/10.1016/j.molstruc.2017.06.125>
13. Muthukumar P, Kim HS, Ku KS, Park JH and Son YA. Synthesis, characterization and aggregation and fluorescence properties of novel highly soluble zinc phthalocyanines bearing tetrakis-4-(3-(piperidin-1-yl)phenoxy) with tetra and dodecachloro substituents (2016) *Fibers Polym* 17: 553-559. <https://doi.org/10.1007/s12221-016-5812-5>
14. Francesconi O, Cicero F, Nativi C and Roelens SA Preorganized hydrogen-bonding motif for the molecular recognition of carbohydrates (2020) *Chem Phys Chem* 21: 257-262. <https://doi.org/10.1002/cphc.201900907>
15. Coubrough HM, van der Lubbe SCC, Hetherington K, Minard A, Pask C, et al. Supramolecular self-sorting networks using hydrogen-bonding motifs (2019) *Chem Eur J* 25: 785-795. <https://doi.org/10.1002/chem.201804791>
16. Herder M, Pätzelt M, Grubert L and Hecht S. Photoswitchable triple hydrogen-bonding motif (2011) *Chem Commun* 47: 460-462. <https://doi.org/10.1039/c0cc02339f>
17. Molodtsova OV, Aristova IM, Potorochin DV, Babenkov SV, Khodos II, et al. 2D/3D metallic nano-objects self-organized in an organic molecular thin film (2020) *ACS Omega* 5: 10441-10450. <https://doi.org/10.1021/acsomega.0c00391>
18. Kimura M, Ueki H, Ohta K, Hanabusa K, Shirai H, et al. Nanoscopic fibrous assemblies made of metallophthalocyanine-terminated amphiphilic polymers (2004) *Chem Eur J* 10: 4954-4959. <https://doi.org/10.1002/chem.200400341>
19. Kimura M, Ueki H, Ohta K, Hanabusa K, Shirai H, et al. Aggregation behavior of amphiphilic phthalocyanine block copolymers (2002) *Langmuir* 18: 7683-7687. <https://doi.org/10.1021/la020275n>
20. Kimura M, Ueki H, Ohta K, Hanabusa K, Shirai H, et al. Preparation of ordered stacked phthalocyanine polymers through olefin metathesis reaction (2001) *Macromolecules* 34: 4706-4711. <https://doi.org/10.1021/ma010163n>
21. Heinrich CD, Tuncel Kostakoğlu S and Thelakkat M. Densely grafted liquid crystalline copper phthalocyanine side chain polymer: synthesis and characterization (2017) *J Mater Chem C* 5: 6259-6268. <https://doi.org/10.1039/c7tc01234a>
22. Wang L, Li J, Zhang W, Chen G, Zhang W, et al. A novel approach to synthesize polymers for potential photodynamic therapy: from benzenedinitrile to phthalocyanine (2014) *Polym Chem* 5: 2872-2879. <https://doi.org/10.1039/c3py01129a>
23. Drager AS, Zangmeister RAP, Armstrong NR and O'Brien DF. One-dimensional polymers of octasubstituted phthalocyanines (2001) *J Am Chem Soc* 123: 3595-3596. <https://doi.org/10.1021/ja004038n>
24. Wöhrlé D. Phthalocyanines in macromolecular phases-methods of synthesis and properties of the materials (2001) *Macromol Rapid Commun* 22: 68-97. [https://doi.org/10.1002/1521-3927\(20010201\)22:2%3C68::aid-arc68%3E3.0.co;2-z](https://doi.org/10.1002/1521-3927(20010201)22:2%3C68::aid-arc68%3E3.0.co;2-z)
25. McKeown NB. Phthalocyanine-containing polymers (2000) *J Mater Chem* 10: 1979-1995. <https://doi.org/10.1039/b000793p>
26. Cook MJ and Heeney MJ. Phthalocyaninohydroannulenes (2000) *Chemistry (Easton)* 6: 3958-3967. [https://doi.org/10.1002/1521-3765\(20001103\)6:21%3C3958::aid-chem3958%3E3.0.co;2-y](https://doi.org/10.1002/1521-3765(20001103)6:21%3C3958::aid-chem3958%3E3.0.co;2-y)
27. High LRH, Holder SJ and Penfold HV. Synthesis of star polymers of styrene and alkyl (meth)acrylates from a porphyrin initiator core via ATRP (2007) *Macromolecules* 40: 7157-7165. <https://doi.org/10.1021/ma062870s>
28. Dichtel WR, Baek KY, Fréchet JMJ, Rietveld IB and Vinogradov SA. Amphiphilic diblock star polymer catalysts via atom transfer radical polymerization (2006) *J Polym Sci Part A Polym Chem* 44: 4939-4951. <https://doi.org/10.1002/pola.21610>
29. de Loos F, Reynhout IC, Cornelissen JJLM, Rowan AE and Nolte RJM. Construction of functional porphyrin polystyrene nano-architectures by ATRP (2005) *Chem Commun* 60. <https://doi.org/10.1039/b412067a>
30. Beil JB and Zimmerman SC. Synthesis of nanosized "cored" star polymers (2004) *Macromolecules* 37: 778-787. <https://doi.org/10.1021/ma034556t>
31. Setaro F, Wennink JWH, Mäkinen PI, Holappa L, Trohopoulos PN, et al. Amphiphilic phthalocyanines in polymeric micelles: a supramolecular approach toward efficient third-generation photosensitizers (2020) *J Mater Chem B* 8: 282-289. <https://doi.org/10.1039/C9TB02014D>
32. Jin Y, Zhang X, Zhang B, Kang H, Du L, et al. Nanostructures of an amphiphilic zinc phthalocyanine polymer conjugate for photodynamic therapy of psoriasis (2015) *Colloids Surfaces B Biointerfaces* 128: 405-409. <https://doi.org/10.1016/j.colsurfb.2015.02.038>
33. Litvinov AL, Kuzmin AV, Yudanov EI, et al. Coordination polymer of manganese(ii) phthalocyanine with 4,4'-bipyridyl: synthesis, crystal structure, and physical properties (2016) *Eur J Inorg Chem* 2016: 5445-5448. <https://doi.org/10.1002/ejic.201600944>
34. Xue C, Chen Z, Luo F-T, et al. Synthesis of water-soluble electroactive ferrocene-grafted poly(p-phenylene-ethynylene) via phase transfer and its biosensing application (2005) *Biomacromolecules* 6: 1810-1815. <https://doi.org/10.1021/bm049231e.s001>
35. Li J and Lindsey JS. Efficient synthesis of light-harvesting arrays composed of eight porphyrins and one phthalocyanine (1999) *J Org Chem* 64: 9101-9108. <https://doi.org/10.1021/jo991102e>
36. Snow AW and Jarvis NL. Molecular association and monolayer formation of soluble phthalocyanine compounds (1984) *J Am Chem Soc* 106: 4706-4711. <https://doi.org/10.1021/ja00329a012>
37. Li J and Kao WJ. Synthesis of Polyethylene Glycol (PEG) derivatives and pegylated-peptide biopolymer conjugates (2003) *Biomacromolecules* 4: 1055-1067. <https://doi.org/10.1021/bm034069j>