# Scalable route to Electroactive and Light active Perylene diimide dye polymer Binder for Li ion Batteries

Pierre Ranque<sup>†,⊥,§</sup>, Chandramohan George<sup>\*,‡,^</sup>, Rajeev K. Dubey<sup>†</sup>, Remco van der Jagt<sup>‡</sup>, Delphine Flahaut<sup>⊥,§</sup>, Rémi Dedryvère<sup>⊥,§</sup>, Marcus Fehse,<sup>‡,∥,§</sup> Panagiotis Kassanos<sup>#</sup>, Wolter F. Jager<sup>\*,†</sup>, Ernst J. R. Sudhölter<sup>†</sup>, Erik M. Kelder<sup>\*,‡,§</sup>.

<sup>†</sup>Delft University of Technology, Faculty of Applied Sciences, Department of Chemical Engineering (OMI-ChemE), Van der Maasweg 9, 2629 HZ, Delft, the Netherlands

^Dyson School of Design Engineering, Imperial College London, SW7 2AZ, London, UK

<sup>‡</sup>Delft University of Technology, Faculty of Applied Sciences, Department of Radiation Science and Technology (SEE-RST), Mekelweg 15, Delft, the Netherlands

<sup>1</sup> IPREM / CNRS / Univ. Pau & Pays Adour / E2S UPPA, Institut des Sciences Analytiques et de Physicochimie pour l'Environnement et les Matériaux – UMR 5254, 64000 Pau, France

<sup>II</sup>Dutch-Belgian (DUBBLE), ESRF-The European Synchrotron, CS 40220, 38043 Grenoble Cedex 9, France <sup>§</sup>ALISTORE-ERI European Research Institute, 33 rue Saint Leu, Amiens, France

# The Hamlyn Centre, Imperial College London, London, UK

\*Email: <u>Chandramohan.George@imperial.ac.uk;</u> <u>W.F.Jager@tudelft.nl;</u> <u>E.M.Kelder@tudelft.nl</u>

# Contents

1. Materials2		
1.1	Chemical synthesis	2
1.2	Electrode process chemicals	2
2. Synthesis		
2.1	Synthesis of compound 1	2
2.2	Polymer synthesis	3
3. Characterizations		5
3.1	Nuclear magnetic resonance	5
3.2	Other characterizations	8
4. Electrochemical measurements		
4.1	Galvanostatic cycling	9
4.2	Cyclic voltammetry	10
4.3	Sheet Resistance Measurements	11

## 1. Materials

## **1.1 Chemical synthesis**

All the chemicals (reagents and solvents) were used as received. The sorbent for the column chromatography was silica gel (technical grade, 40-63  $\mu$ m -230-400 mesh- particle size), purchased from commercial suppliers.

Reagents:

p-Toluenesulfonic acid monohydrate  $\geq$  98.5%, CAS number 6192-52-5, Sigma Aldrich. 2-ethyl-1-hexylamine 98%, CAS number 104-75-6, Sigma Aldrich. 6-amino-1-hexanol 97%, CAS number 4048-33-3, Sigma Aldrich. Pyridine anhydrous 99.8%, CAS number 110-86-1, Sigma Aldrich. 4-(Dimethylamino)pyridine  $\geq$  99%, CAS number 1122-58-3, Sigma Aldrich. Methanol, anhydrous, 99.8%, CAS number 67-56-1, Sigma Aldrich. Poly(acryloyl chloride),25% in Dioxane, CAS number 25189-84-8, ABCR.

Solvents:

Toluene technical grade, CAS number 108-88-3, FMVG.

Dichloromethane anhydrous  $\geq$  99.8%, CAS number 75-09-2, Sigma Aldrich.

### **1.2 Electrode process chemicals**

PVdF-HFP copolymer Solef 21216, Solvay.

1-methyl-2-pyrrolidinone anhydrous 99.5%, CAS number 872-50-4, Sigma Aldrich. Carbon black Super C45, TIMCAL. Lithium ribbon 99.9% trace metal basis, CAS number 7439-93-2, Sigma Aldrich.

Lithium hexafluorophosphate solution, 1.0 M LiPF<sub>6</sub> EC/DMC 50/50 (v/v), Sigma Aldrich.

## 2. Synthesis

## 2.1 Synthesis of compound 1



Synthesis of compound 1 was carried out by following the previously described procedure (*Org. Chem. Front.*, **2016**, *3*, 1481-1492). However, herein, we did not purify the compound 1 and used it as crude in the next step. This helped to prevent the loss caused by recrystallization. Moreover, the repeated recrystallization of tetrachloro-PTBE (step 2) was relatively more efficient at higher quantity and, therefore,

we could increase the yield up to 90 % for this step. In this way, herein, we were able to achieve compound 1 with higher overall yield (ca. 67%) as compared to the previously reported procedure (reference 19).



#### 2.2 Polymer synthesis

Figure S1. Synthesis pathway leading to the production of our analogous polymer.

The synthesis of compound 4, starts with the imidization of 1,6,7,12-tetachloroperylene-3,4,9,10-tetracarboxy monoanhydride dibutylester (1), a compound that is readily available from commercially available PDA in three reaction steps. Deprotection of ester functionalities of the perylene monoimide diester (2), followed by an imidization with 6-hydroxy-hexylamine yielded the desired monohydroxy PDI (compound 4). This reaction has been executed on a 9 gram scale using starting material that contained 10% of 1,6,7,12-tetachloro-PDA, which was formed as a side product during the synthesis of precursor 1. Removal of tetrachloro-PDA from starting compound 1 is possible, but starting the synthesis of compound 4 with contaminated starting material and doing the purification in the very last steps is the more efficient approach. Indeed, this contaminant did not harm any of the subsequent reactions and the symmetric bis(2-

ethylhexyl)-tetrachloroperylene diimide that was formed from it, was easily removed by column chromatography in the last step.

Synthesis of N-(2-Ethyl-1-hexyl)-1,6,7,12-Tetrachloroperylene-3,4,9,10-tetracarboxy Monoimide Dibutylester (2): Compound 1 (9.15 g, 12.72 mmol), containing 10 mol% of tetrachloroperylene dianhydride, was taken in 200 mL toluene. Then, 2-ethyl-1-hexylamine (6.81 mL, 41.58 mmol) was added and the reaction was stirred 16 h at reflux. Afterwards, the solution was cooled down to room temperature and toluene was removed via rotavap. The remaining solid was washed with several portions of water and methanol on a glass filter. A column chromatography on silica gel was performed with dichloromethane to completely remove amine impurities. The final crude compound (10.46, g) was containing 9.42 g of 2 (i.e. yield of 96%) and 10 mol% of N,N'-di-(2-ethyl-1-hexyl)-1,6,7,12-tetachloroperylene diimide side product, which was formed by imidization of the tetrachloroperylene dihanydride impurity. For characterization purpose, a column chromatography on silica gel was performed with a 2:1 dichloromethane-hexane mix as eluent. The migration speed of the products was nearly similar, but a fraction of pure compound 2 was successfully isolated to carry out NMR. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta = 8.63$  (s, 2H), 8.13 (s, 2H), 4.43-4.33 (m, 4H), 4.20-4.10 (m, 2H), 1.99-1.90 (m, 1H), 1.85-1.78 (m, 4H), 1.56-1.47 (m, 4H), 1.43-1.31 (m, 8H), 1.02 (t, J = 7.4 Hz, 6H), 0.97-0.88 ppm (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 166.8, 162.8, 134.6, 100$ 134.3, 133.7, 132.8, 132.1, 131.5, 129.2, 126.5, 123.4, 123.0, 122.6, 66.2, 44.5, 38.0, 30.7, 30.5, 28.7, 24.0, 19.2, 14.1, 13.8, 10.6 ppm.

Synthesis of *N*-(2-Ethyl-1-hexyl)-1,6,7,12-Tetachloroperylene-3,4,9,10-tetracarboxy Monoimide Monoanhydride (3): Crude compound 2 (17.6 g, 22.81 mmol) was mixed with *p*-TsOH·H<sub>2</sub>O (21.70 g, 114.06 mmol) and toluene (250 mL). The reaction was carried out for 24 h at reflux. Then, toluene was removed under vacuum. The solid was washed with water and methanol under glass filter. Due to the high scale, *p*-TsOH impurities were difficult to remove. Several dissolutions in dichloromethane and precipitation in methanol were done. The final compound (14 g, 96%), still contains 10 mol% of *N*,*N*'-di-(2-ethyl-1-hexyl)-1,6,7,12-tetrachloroperylene diimide.

Synthesis of *N*-(6-Hydroxyhexyl)-*N*'-(2-Ethyl-1-hexyl)-1,6,7,12-tetrachloroperylene-3,4,9,10tetracarboxy Diimide (4): Compound 3 (9.73 g, 15.17 mmol), containing 10 mol% of the *N*,*N*'-di-(2ethyl-1-hexyl) tetrachloroperylene diimide impurity, and 6-amino-1-hexanol (5.3 g 45.23 mmol), were taken in 250 mL of toluene. The solution was stirred for 16 h under reflux. Afterward, the mixture was cooled down to room temperature and the solvent was removed under vacuum. The solid was solubilized in dichloromethane and a column chromatography on silica gel was performed. First dichloromethane was used, as eluent, to easily remove the impurity of *N*,*N*'-di-(2-ethyl-1-hexyl)-1,6,7,12-tetrachloroperylene diimide. Then, chloroform was used to obtain pure compound 4 (8.58 g, 76%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta = 8.66$  (s, 4H), 4.21 (t, *J* = 7.4 Hz, 2H), 4.17-4.09 (m, 2H), 3.68 (t, *J* = 6.5 Hz, 2H), 1.99-1.90 (m, 1H), 1.81-1.73, (m, 4H), 1.66-1.59 (m, 2H), 1.50-1.46 (m, 4H), 1.42-1.31 (m, 8H), 0.97-0.88 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 162.5$ , 162.2, 135.3, 135.2, 132.9, 132.9, 131.3, 128.6, 128.4, 123.2, 123.2, 123.1, 62.7, 44.5, 44.7, 37.9, 32.5, 30.6, 28.6, 27.9, 26.7, 25.3, 23.9, 23.0, 14.1, 10.5.

**Synthesis of the analogous polymer 6:** In a dried flask, pure compound **4** (4.00 g, 5.40 mmol) was solubilized in 100 mL dry dichloromethane under an argon atmosphere. To this was subsequently added DMAP (0.033 g, 0.27 mmol), pyridine (2.7 mL, 33.39 mmol) and the poly(acryloyl chloride) 25% solution in dioxane (1.9 mL, 5.40 mmol of acryloyl chloride group). The solution was mixed 72 h at room temperature. To quench the reactivity of the compound **5** obtained, an excess of dry methanol was added (4 mL, 98.88 mmol). The mixture was stirred 2 more hours at room temperature. Then, the solution was precipitated in methanol and filtrated over a filter paper. The purification of the polymer was done by repeated precipitation from chloroform into acetone. The final pure compound **6** (2.03 g) was achieved with a grafting degree of **4** estimated at 75-80%.

# 3. Characterizations

### 3.1 Nuclear magnetic resonance

The NMR spectra were recorded with a 400 MHz pulsed Fourier transform Agilent-400 MR DD2 spectrometer in commercial CDCl<sub>3</sub> (99.8 at% D, containing 0.1 vol% TMS). The chemical shifts are quoted relative to Tetramethylsilane for <sup>1</sup>H NMR ( $\delta = 0.00$ , singlet) and CDCl<sub>3</sub> for <sup>13</sup>C NMR ( $\delta = 77.00$ , triplet), at room temperature.

Proton NMR



Figure S2. Proton NMR of compound 2 at the top and compound 4 at the bottom, in CDCl<sub>3</sub>.



Figure S3. Proton NMR of the final polymer (compound 6), in CDCl<sub>3</sub>.

% perylene grafted = 
$$\frac{(\int a + b)/4}{\frac{\int a + b}{4} + \frac{\int \delta}{3}} \times 100 = \frac{4.1/4}{\frac{4.1}{4} + \frac{0.3}{3}} \times 100 \approx 77 \pm 2\%$$

Calculation of the theoretical Mn of this analogous polymer (compound 6):

The commercial poly(acryloyl chloride) used has an average Mn of 9000 to 10000 g mol<sup>-1</sup>. Since the acryloyl chloride has a molecular weight of 90.506 g mol<sup>-1</sup>, we can deduct that a polymer chain contains at least 99 side functions.

From the proton NMR of our polymer, we know that at least 75% of the side groups are composed of perylene diimide (*n.b.* the molecular weight of this part is 794.55 g mol<sup>-1</sup>), and the other 25% are methyl acrylate groups (*n.b.* the molecular weight of this part is 86.09 g mol<sup>-1</sup>).

So, the minimal theoretical Mn = 74 x 794.55 + 25 x  $86.09 \approx 60900$  g mol<sup>-1</sup>.

# APT <sup>13</sup>C NMR



Figure S4. APT <sup>13</sup>C NMR of compound 2 at the top and compound 4 at the bottom, in CDCl<sub>3</sub>.

## 3.2 Other characterizations

Simultaneous small-angle X-ray scattering and wide-angle X-ray scattering (SAXS and WAXS) measurements were performed at beamline BM26B28 at the European Synchrotron Radiation Facility (ESRF) in Grenoble with a wavelength  $\lambda = 1.00$  Å.<sup>1,2</sup> Acquisition of simultaneously SAXS and WAXS patterns was performed over time intervals of 30 seconds using a Pilatus 1M detector (981 × 1043 pixels of 172 µm × 172 µm placed at a distance of 1.5 m) and a Pilatus 300K detector (1472 × 195 pixels of 172 µm × 172 µm placed at a distance of 0.28 m), respectively. The scattering vector q is defined as  $q = 4\pi/\lambda$ (sin  $\theta$ ) with 2 $\theta$  being the scattering angle.

The crystal structures of the prepared electrodes were analyzed by X-ray powder diffractions (XRD) by using a Panalytical X'Pert Pro PW3040/60 diffractometer with a Cu K $\alpha$  radiation source operating at 45 kV and 40 mA.

The absorption spectrum was recorded at room temperature in  $CH_2Cl_2$  with a standard double beam UV-Vis spectrophotometer.

Thermogravimetric analysis (TGA) was performed on PPDI to determine its thermal stability. The result obtained in Figure S5, was performed with the analyzer TGA Q50 V6.7 Build 203, under air flow, at 20 °C min<sup>-1</sup>.



Figure S5. TGA spectrum of polymer 6, done under air flow.

## 4. Electrochemical measurements

Commercial samples of lithium ion phospahte (LFP) were used as active material. Perylene diimide (PPDI) based slurries of commercial LFP, carbon black (CB, TimCal) and PPDI were dispersed in 1:1 volum ratio of N-methyl-2-pyrrolidone/Chlorobenzene (Sigma-Aldrich) and casted on aluminium foil. PVdF-based

<sup>&</sup>lt;sup>1</sup> M. Borsboom, W. Bras, I. Cerjak, D. Detollenaere, D. Glastra van Loon, P. Goedtkindt, M. Konijnenburg, P. Lassing, Y. K. Levine, B. Munneke, M. Oversluizen, R. van Tol, E. Vlieg, *J. Synchrotron Rad.*, **1998**, *5*, 518.

<sup>&</sup>lt;sup>2</sup> W. Bras, I. P. Dolbnya, D. Detollenaere, R. van Tol, M. Malfois, G. N. Greaves, A. J. Ryan, E. Heeley, *J. Appl Cryst.*, **2003**, *36*, 791.

slurries of LFP, CB and polyvinylidene fluoride (PVdF, SOLEF) were dispersed in NMP. The electrodes were dried in an oven at 80°C (which resulted in an active mass loading of 2-3 mg/cm<sup>-2</sup>). The LFP-electrodes (working electrode) were assembled in custom-built Swagelok cells in an Argon-filled glovebox (MBraun). Lithium metal (Sigma-Aldrich) and glassfiber were used as counter/reference electrode and separator, respectively. A standard 1M LiPF<sub>6</sub> in ethylene carbonate and dimethyl carbonate (1:1 vol) solution (Sigma-Aldrich) was used as electrolyte.

#### 4.1 Galvanostatic cycling

Electrochemical cycling of the batteries were performed on a M4000 Maccor battery tester between 2.5 and 4.0 V vs Li<sup>+</sup>/Li at 1C and 0.1C-rates, based on the LFP-capacities of the electrodes (170 mAh  $g^{-1}$ ).



**Figure S6**. a-b) Charge/discharge curves of PVdF-based electrode (80% LFP, 10% CB and 10% PVdF) at C/10 (a) and 1C (b). d) Galvanostatic mesurments at 1C of LFP/CB/PPDI (80/2/18 wt%) and LFP/CB/PVdF (80/10/10 wt%).

Using only 2 wt% of carbon black in LFP/PVdF electrodes leads to very poor performance at C/10, see Figure S7. It can be seen that the polarisation (overpotential) is high for this electrode (>0.65V compared to ~0.21V of PPDI based electrodes), most likely due to poor electronic conduction since electrodes with mass ratio of 80/10/10 do not suffer from this, (see figure S6a). Also, the stability is very poor since these batteries lost their capacity after only 4 cycles, and reached no capacity within 20 cycles.



**Figure S7**. Electrochemical performances of LFP/CB/PVdF (80/2/18 wt.%) at C/10. a) Charge/discharge profiles of cycle #1,2,3 & 6. b) Cycle performance at C/10 of two different electrodes with this same composition (*i.e.* 80/2/18 wt.% of LFP/CB/PVdF).

#### 4.2 Cyclic voltammetry

Cyclic voltammetry tests of LFP based electrodes were performed on a potentiostat/galvanostat (PGSTAT302N, Metrohm) at 0.05 mV s 1 (first CV-cycle) and 0.1 mV s-1 in the voltage range 2.5-3.8 V vs Li<sup>+</sup>/Li.



**Figure S8**. Cyclic voltammetry curves (2<sup>nd</sup> cycle) of perylene diimide (PPDI)-based (a) and PVdF-based (b) electrodes, at a scan rate of 0.1 mV s<sup>-1</sup>.

Electrochemical cycling of pure PPDI casted on Al foil was performed in half cells on a potentiostat/galvanostat (PGSTAT302N, Metrohm) at 0.05 mV s in the voltage range between 2.0 - 5 V vs  $Li^+/Li$ , to determine its electrochemical stability.



Figure S9: CV performed using pure PPDI on aluminium foil as electrode vs. solid lithium. This CV data show the first four cycles obtained between 2 and 5 V vs.  $Li^+/Li$ , at 0.5 mV/s.

This CV shows several interesting features. First, our polymer has a reversible electrochemical activity around 2.65 V vs. Li<sup>+</sup>/Li. Second, the polymer seems to be stable until at least 3.9 V vs. Li<sup>+</sup>/Li. Above that voltage some irreversible oxidations occur but the redox activity of our polymer remains reversible.

#### 4.3 Sheet Resistance Measurements

Instrumentation: Sheet resistance measurements were carried out by using a Keithley SCS4200A semiconductor analyser system having four source meter units (SMU). Four manual micromanipulators (PVX 500, Wentworth Laboratories, Bedfordshire, UK) were equipped with tungsten needle probes (5101-14041, Wentworth Labs, Bedfordshire, UK), resting on the samples for measurements. Sample imaging which guides the correct positioning the probes was carried out by using a digital microscope (VHX-2000, Keyence, Osaka, Japan). One SMU applies  $\sim 10 \mu A$  constant current, while the second one provides a ground for current sinking and two other SMUs record the voltage. The resistance is obtained by dividing the potential difference between the two probes by the current applied, which is further divided by  $\pi/\ln(2)$ for calculating sheet resistance. Figure S10(a) shows the experimental setup, where equidistant between probes was maintained (350  $\mu$ m), as shown in Figure S10(b). The setup was housed on optical table, where the micromanipulators were positioned by vacuum. This enables four-point (Kelvin) measurements via removal of lead resistance from measurements and the contact impedance between metal probe and sample (battery slurry coatings). Possibly, contact impedance can be greater than the actual resistance of the samples and the voltage across the current-carrying terminals was monitored. If contact impedance is greater than SMU voltage compliance (for applied current value), this can lead to misleading readings. Measurements were conducted at different locations on each sample and 26 readings were collected at each location over 200 s, as shown in Figure 10 (b) and (c). For PVDF/LFP sample, an average sheet resistance of 640 $\Omega/\Box$  was calculated with a standard deviation of 113  $\Omega/\Box$ . For PPDI/LFP sample, the average sheet resistance was 313  $\Omega/\Box$  with a standard deviation of 150/ $\Box$ .



**Figure S10.** (a) The experimental setup for sheet resistance measurements. (b) Probe separation and placement on a sample. Sheet resistance measurements over time at different locations for electrodes containing 2% carbon (c) PVDF/LFP (avg. 640  $\Omega/\Box$ ) and (d) PPDI/LFP (avg. 313 $\Omega/\Box$ ).