Design and Synthesis of Polymer Supramolecular Functional Nanomaterial

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Supramolecular chemistry has emerged as a promising approach for functional nanomaterials. The challenge of the area is how to synthesize self-assembled objects in a designed fashion in terms of particles shapes, chemical compositions and architectures, etc. We are trying to address this challenge using polymers, especially block copolymers, as self-assembly building blocks. As a result, a number of nanomaterials with designed chemical compositions have been prepared. Particularly, we have developed new concepts to incorporate metal elements into polymer nanoparticles in an attempt to develop nanomaterials possessing magnetic, conductive, optical, catalytic properties for potential applications. This talk will briefly summarize our efforts in this area.

Synthesis and Self-Assembly of Metal-Containing Polymer for Supramolecular Functional Nanomaterials

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Outline

I. Research interests

II. Polymer supramolecular chemistry

III. Metal-containing polymer and supramolecular chemistry

IV. Metal coordination polymer nanoparticles
   1. designed synthesis
   2. functions and properties

IV. Summary

V. Acknowledgement

Polymer Supramolecular Functional Nanomaterials

Polymer synthesis ← 1) Living free radical polymerization 2) Organometallic and metal coordination chemistry

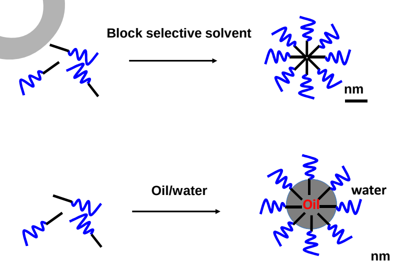
↓

Supramolecular chemistry → 1) Defined synthesis 2) Multicomponent systems

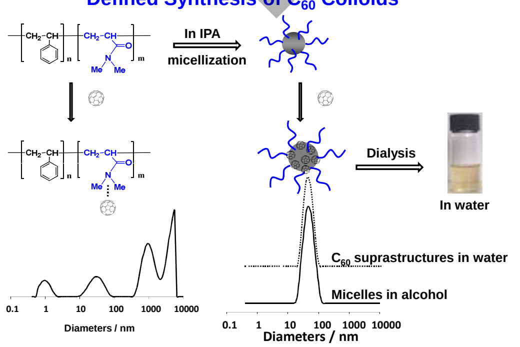
↓

Functions and material applications → 1) metal elements, e.g. electronic, optical, catalytic, etc. 2) polymers, e.g. stimulus, solubility, mechanical properties, etc. 3) nanostructures and synergetic effects of nanodomains, e.g. porous network, charge transfer, smart materials, etc.

Polymer Solution Self-Assembly

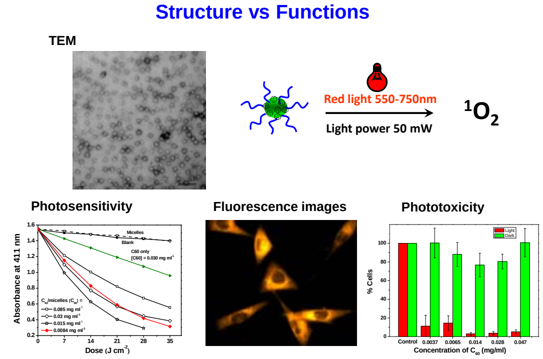


Polymer Supramolecular Chemistry
Defined Synthesis of C_{60} Colloids



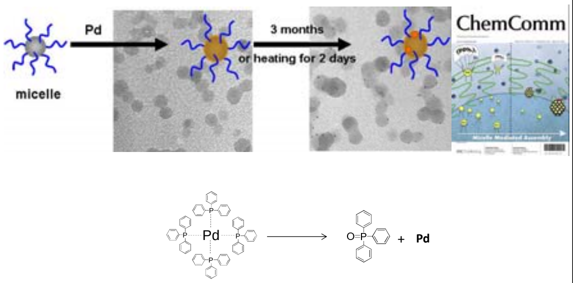
Wang, X. S.; Metanawin, T.; Zheng, X. Y.; Wang, P. Y.; Ali, M.; Vernon, D., *Langmuir* 2008, 24, 9230-9232.

Polymer Supramolecular Chemistry
Structure vs Functions



Tanapak Metanawin, Tian Tang, Rongjun Chen, David Vernon and Xiaosong Wang Nanotechnology 2011

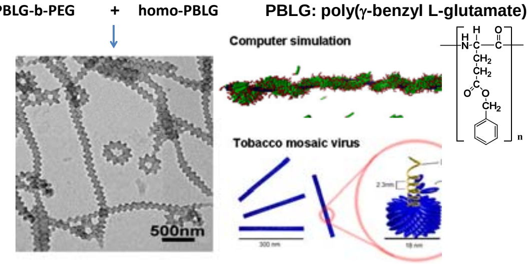
Polymer Supramolecular Chemistry
Adjusting Nucleation Rate



Polymer Supramolecular Chemistry
for Novel Morphology

PBLG-b-PEG + homo-PBLG

PBLG: poly(γ-benzyl L-glutamate)



Cai, C. H.; Lin, J. P.; Chen, T.; Wang, X. S.; Lin S. L. *Chem. Commun.* 2009 2709-2711.

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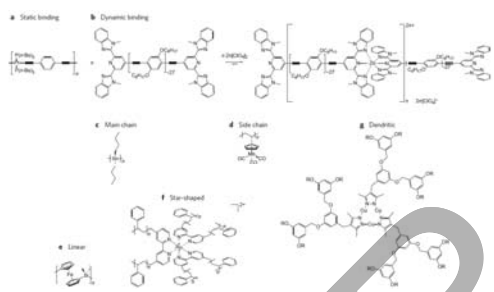
Examples of Metal Containing Polymers

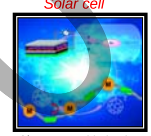


From organometallic and polymer chemistry to processible materials

Nature Material 2011 176

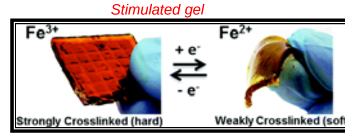
Metal Containing Polymers Materials

Solar cell



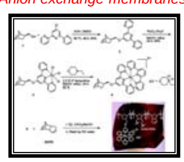
Acc. Chem. Res., 2010, 43 (9),1246–1256

Stimulated gel



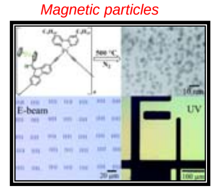
ACS Macro Lett., 2012, 1 (1), pp 204–208

Anion exchange membranes



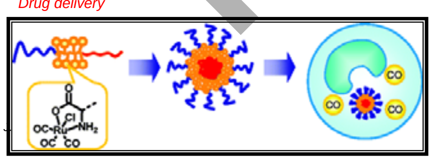
J Am Chem Soc. 2012, 134, 4493

Magnetic particles



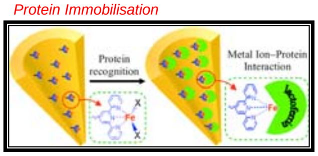
Angewandte Chemie International Edition 2008, 47, 1255–1259.

Drug delivery



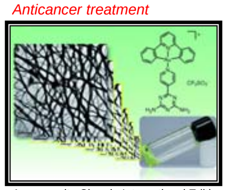
J. Am. Chem. Soc., **2010**, *132* (51), pp 18273–18280

Protein Immobilisation



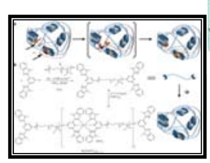
J. Am. Chem. Soc., 2011, 133 (43), pp 17307–17314

Anticancer treatment



Angewandte Chemie International Edition 2012 early view

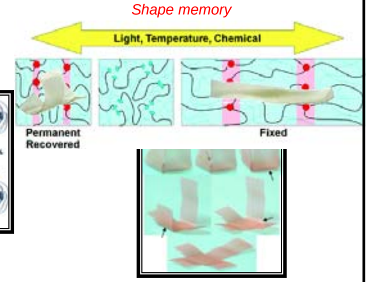
Optical healing



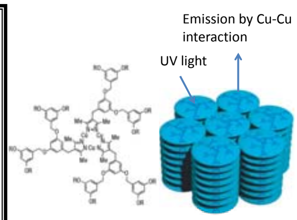
Nature 472, 334–337

http://www.nature.com/nature/journal/v472/n7343/extref/nature09963-s2.mpg

Shape memory



J Am Chem Soc. 2011 Aug 17;133(32):12866-74.



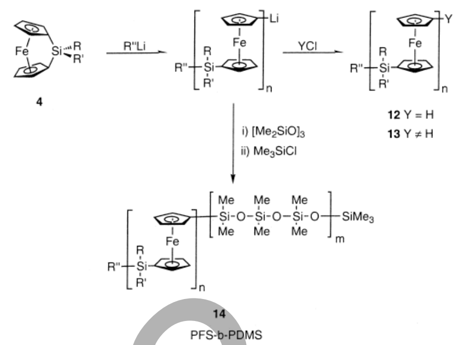
The photographs were taken at room temperature: a, under room light. b–d, on exposure to a 254-nm ultraviolet light. Procedures:

1. **(i) Printing with a thermal facsimile-type printer.**
2. **(ii) Heating at 100 °C for blacking out.**
3. **(iii) Aging at 45 °C for initialization.**

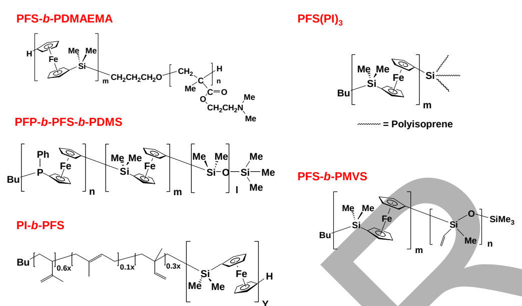
Security ink

Nature Mater. 4, 546–549 (2005).

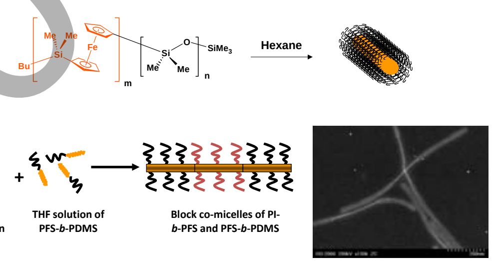
Anionic Living Polymerization for Metal-Containing Polymer Synthesis



Metal Containing Polymer Architecture Design

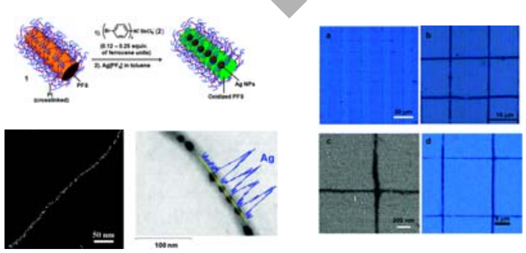


Living Self-Assembly for Block Comicelles



Wang, X. S; Guerin, G.; Wang, H.; Wang, Y. S.; Manners, I.; Winnik, M. A. Science 2007, 317, 644-647.

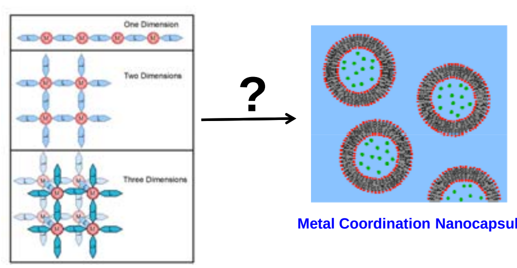
Nanomaterials From PFS Micelles



J. Am. Chem. Soc. **2005**, *127*, 8924 and **2008,** *130*, 12921–12930.

J. Am. Chem. Soc., **2007**, *129* (17), 5630–5639. and **2003**, *125*, 12686−12687

Supramolecular Chemistry for Processible Metal-Coordination Polymers and Nanoparticles

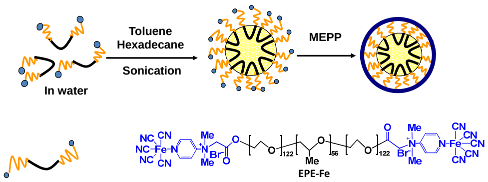


Metal Coordination Nanocapsules

Rich functionalities associated with metal ions, organic ligands and porous structures

But lack of techniques for designed synthesis, …

Sequential Self-assembly of Block Copolymers and Metal Ions for Designed Synthesis of Metal Coordination NanoShells



- Rational structure design, e.g. size, shape, chemical composition
- Efficient encapsulation,
- Functional hybrid nanoshells

G. Liang, J. Xu and X. Wang, J. Am. Chem. Soc. 2009, 131, 5378–5379

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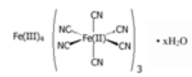
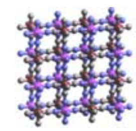
Prussian Blue and Its Analogues



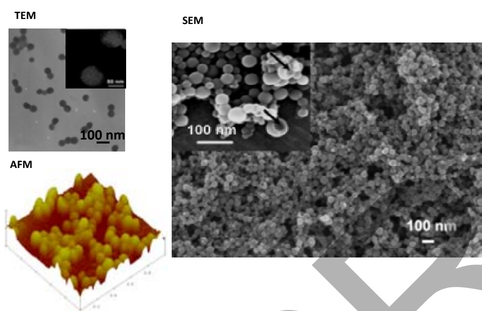


Radiogardase® For Oral Administration
very high affinity for radioactive and non-radioactive cesium and thallium.

Oxidase-enzyme-based biosensors.

Magnetic properties of PB analogues: e. g. light-induced magnetic switch

Microscopy Characterization of PB Nanoshells



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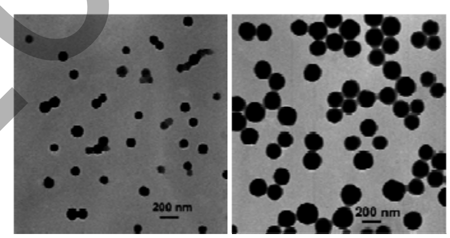
PB Nanosells with Varied Size



0.5 % surfactants, 5% toluene   0.5% surfactants, 20% toluene

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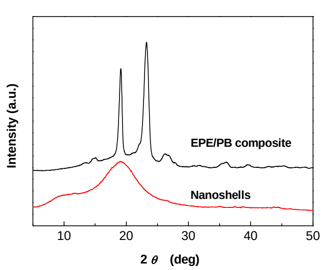
Amorphous Nature of the PB NanoShells



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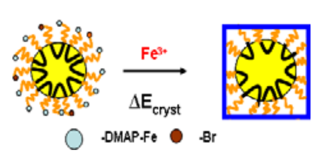
Nanoshells with Crystalline Structures



Surfactants: 4 wt%, containing 60 % of –DMAP-Fe end groups

Oil (toluene) content: 5 wt%.

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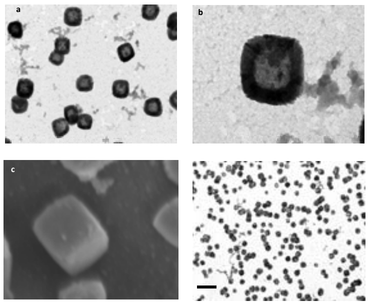
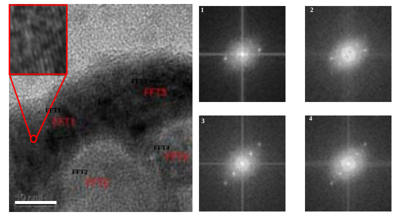
TEM and SEM Images of the Nanoboxes

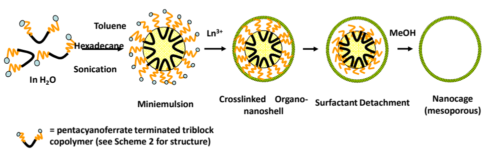


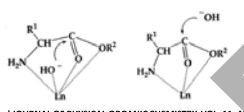
R. McHale, N. Ghasdian, Y. b. Liu, M. B. Ward, N. S. Hondow, H. H. Wang, Y. Q. Miao,c R. Brydsonb, X. S. Wang, Chem. Commun., 2010, Hot Article!

Crystallinity of the Nanoboxes



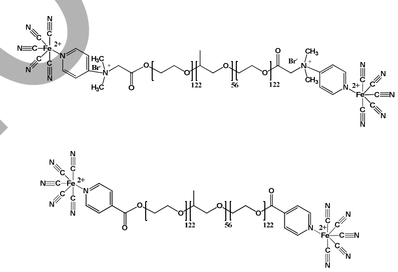
Dual Lanthanide Role in the Designed Synthesis of Prussian Blue Analogue Nanocages





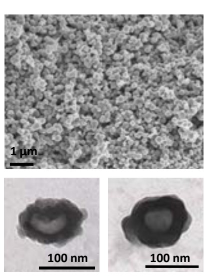
Makoto Komiyama et al JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 11, 41–46 (1998)

MetalloSurfactant Design for the Synthesis of Nanocages



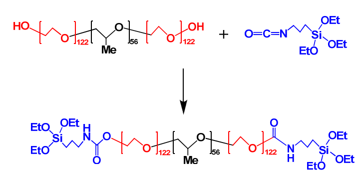
Noemí D. Lis de Katz a and Néstor E. Katz Monatshefte für Chemic 113,745--750 (1982)

SEM and TEM of PB analogue Nanocages

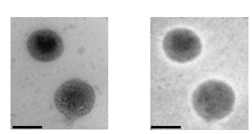


Gd@PB Er@PB

Synthesis of Silica Nanocapsules

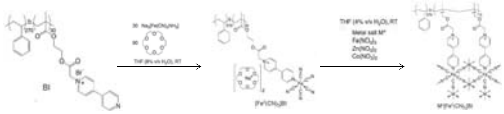


TEM analysis:
(Contrast was provided by selectively staining encapsulated dyes using OsO_4)

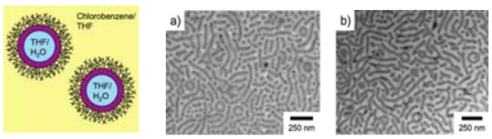


Carbon element mapping

Block Copolymer Assisted PB Nanoparticle Synthesis



bipyridinium-functionalized block ionomer (BI)



X. Roy, J. K.-H. Hui, M. Rabnawaz, G. Liu and M. J. MacLachlan, J. Am. Chem. Soc., 2011, 133, 8420–8423.; Angew. Chem. Int. Ed. 2011, 50, 1597 –1602

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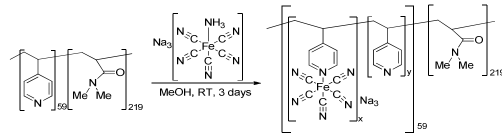
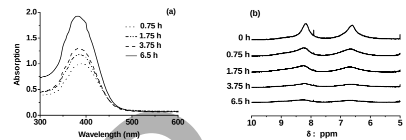
Pentacyanoferrate-Coordinated Block Copolymers

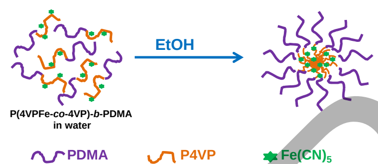


UV

NMR



Micellization of Pentacyanoferrate-Coordinated Block Copolymers



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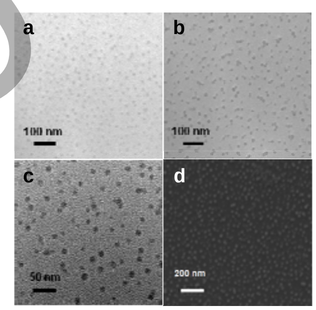
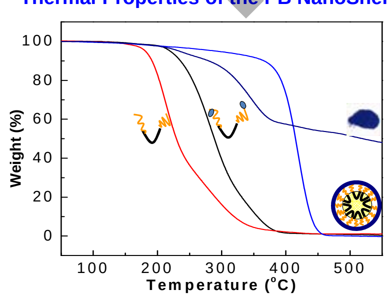
Electron Microscope Images



PB nanoparticles: uniform morphology and size, soluble in water and organic solvents

Thermal Properties of the PB NanoShells



Higher thermostability of PB nanoshells;
The organo-nanoshells comprise >90 wt% organic surfactant in their interior.

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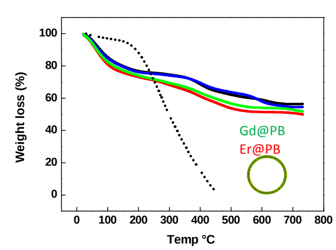
Thermal Behaviour of the Nanocages



The nanocages consist of pure metal coordination polymers

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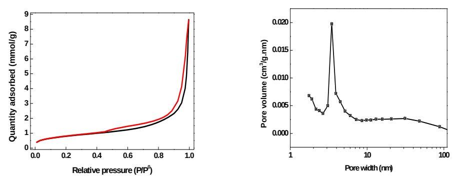
Nanocages with Mesoporous Walls

N_2 gas adsorption (black) /desorption (red) isotherm (left) for Er@PB nanocages and the concomitant pore size distribution curve (right).



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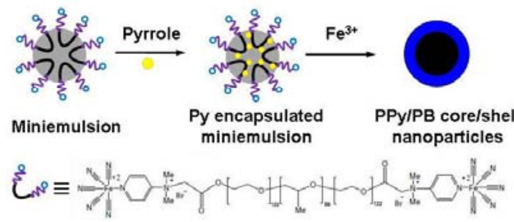
Synthesis of Core/Shell PB Nanoparticles



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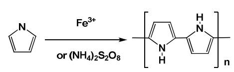
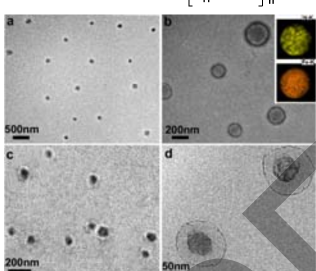
PPy/PB Core/Shell Nanoparticles





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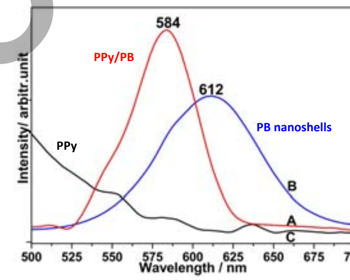
Photoluminesence of PB Nanoshells and PPy/PB Core-Shell Nanoparticles



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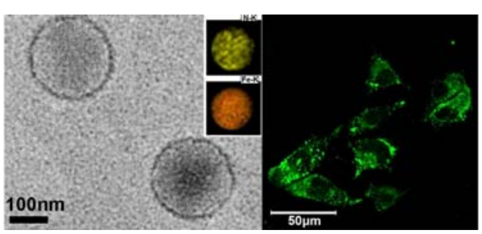
Photoluminescence of PPy/PB Core/Shell Nanoparticles inside Cells



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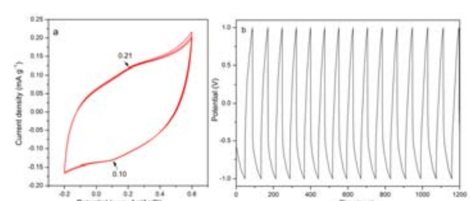
Electronic Properties of PPy/PB Core-Shell Nanoparticles

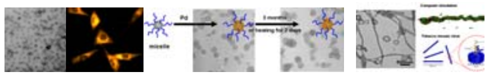


The specific capacitance of the electrode is calculated to be 187.5 Fg^{-1}

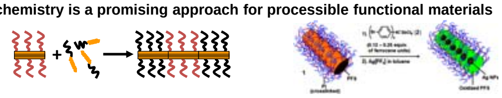
Summary

We strive to develop functional materials via supermolecular, polymer and organometallic chemistry

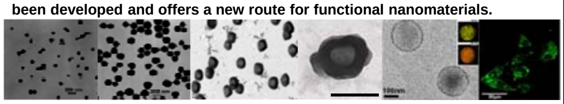
I) Explored the potential of polymer supramolecular chemistry.



II) Polymer chemistry combined with metal coordination and organometallic chemistry is a promising approach for processible functional materials



III) Designed synthesis of metal coordination polymer nanoparticles has been developed and offers a new route for functional nanomaterials.



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Acknowledgments

- Dr. Guodong Liang, Dr Ronan McHale, Ms YiBo Liu, Ms Sunjie Ye, Ms Negar Ghasdian, Mr Tanapak Metanawin, Dr. Tian Tang.
- Dr. David Vernon and Dr Rongjun Chen at Leeds for cell studies.
- Dr. Patrick McGowan at Leeds for Pd self-assembly studies.
- Dr. Jiaping Lin at ECUST for peptide block copolymer self-assembly
- Dr. YunLu at Nanjing University for conducting polymer/PN core/shell nanoparticles
- EPSRC, NESRC and University of Waterloo for financial support.

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