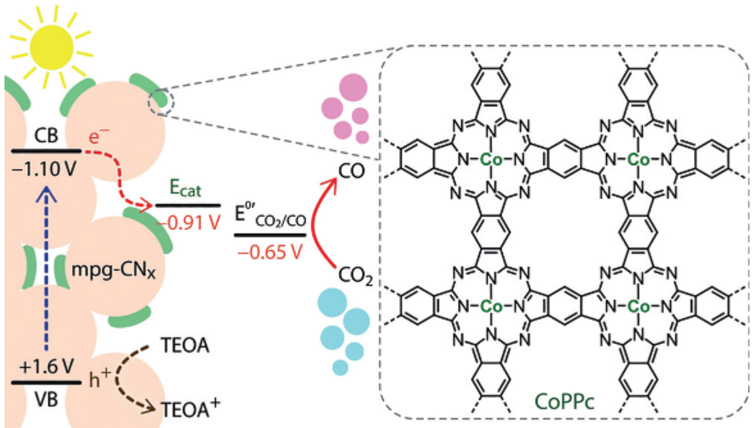

Figure 1.24 Schematic illustration of light-driven CO_2 reduction property and electronic structures of mpg-CN_x@CoPPc hybrid. Source: Ref. [260] / John Wiley & Sons / CC BY 4.0.

efficiency and recycling stability for the aerobic oxidation of arylalkanes. The conversion efficiency and selectivity of ethylbenzene were able to reach 95% and 99%, respectively. In 2019, a precious metal-free composite composed of CoPPc and mesoporous carbon nitride (mpg-CN_x) as the photosensitizer was assembled, selectively converting CO_2 to CO with a turnover number of 90 based on an active cobalt site after 60 hours (Figure 1.24) [260].

1.5.4 Phthalocyanine-Based Polymeric Materials for Energy Storage

The exploration of sustainable and safe alternative energy sources and storage devices is highly desirable in modern society. LIBs with higher energy and power densities have been widely used as recharged devices in daily life and industry. Their theoretical capacity was restricted by anode and cathode electrode materials, such as $LiFePO_4$ and graphite, respectively. In order to pursuit higher energy density, metal–air batteries (MABs) such as Li-O_2 and Zn-O_2 batteries were established to replace the intercalation mechanism in LIBs with the redox reaction between the metal and oxygen. For the development of such technologies, efficient and stable electrocatalysts are vital to accelerate the slow kinetics of redox reactions that occur at the electrode surface. MPcs constitute one kind of promising M-N_4-type molecular electrocatalysts with outstanding activity toward H_2, O_2, and CO_2 electrocatalysis. The electrocatalysis results of ORR and CO_2RR are briefly mentioned in the previous section. Now, the rechargeable Li-CO_2 battery technology upon polyphthalocyanine has been introduced as a representative of MAB. Instead of O_2, atmospheric CO_2 has been used as the energy carrier for this kind of MABs. Low-cost conjugated CoPPc has been demonstrated to exhibit good catalytic activity to reversibly form and decompose Li_2CO_3 [261]. CoPPc was obtained from the microwave heating reaction of 1,2,4,5-tetracyanobenzene and Co^{2+}. A *N*-methylpyrrolidone (NMP) suspension of CoPPc was deposited on a carbon cloth to assemble Li-CO_2 battery. The good catalytic activity of CoPPc ensures the device with a high areal capacity of 13.6 mA h cm^{-2} and rate performances. In addition to the MABs, Pc-based polymeric materials have been used in different metal-ion batteries. For example, sodium-ion batteries (SIBs) have been proposed as a kind of next-generation energy storage device. Metallic polyphthalocyanines (MPPcs) due to the N-rich conjugation structure have been attempted as the SIBs' anode [262]. Molten salt reaction of tetracyanobenzene in the presence of $FeCl_2$, $Co(OAc)_2$, $Ni(OAc)_2$, and $Cu(OAc)_2$ at 350 °C under Ar generates MPPc (M = Fe, Co, Ni, and Cu). The coin-type cells fabricated by MPPc show high capacities up to 538 and 342 mA h g^{-1} at 50 and 1000 mA g^{-1}, respectively. In particular, their rate performance and cycling performances are similar to those of the excellent anode materials of SIBs.

1.6 Conclusion

In this chapter, we intend to summarize as much as contributions toward the construction of Pc-based functional polymeric materials mainly including coordination polymers and covalent organic polymers with well-defined structures, rather than those amorphous supramolecular nanostructural assemblies. In particular, we introduced the versatile chemistry from Pc-based monomer, oligomer, and polymeric materials including MOFs and COFs, making possible correlation between structures and functions at the basic and precise molecular levels. In addition, the preparation of functional monomeric macrocycles and the controlled organization of polymeric structures were presented. Finally, some examples of Pc-based polymeric materials were also displayed for their practical applications.

Abbreviations

AQ	Anthraquinone
ATRP	Atom transfer radical polymerization
BBTC	bBenzo[1,2-b:4,5-b′]bis[1,4]benzodioxin-2,3,9,10-tetracarbonitrile
BET	Brunauer–Emmett–Teller
C_{60}	Fullerene
CGSs	Chemiresistive gas sensors
CO_2RR	Carbon dioxide reduction reaction
COFs	Covalent–Organic Frameworks
D-A	Donor–Acceptacceptor
D-A-D	Donor–Acceptacceptor–Donordonor
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DMA, DMAc	Dimethylacetamide
DMF	*N*,*N*-dimethylamino
DMSO	Dimethyl Sulfoxidesulfoxide
FE_{CO}	CO Faradaic efficiency

FTO	Fluorine-doped tin oxide
HMDS	Hexamethyl Disilazane
HOFs	Hydrogen-Bonded Organic Frameworks
HR-TEM	High -resolution transmission electron microscopy
IC_{50}	Inhibitory Concentration
M	Metal
MABs	Metal–Air Batteries
MOCs	Metal–Organic Cages
MOFs	Metal–Organic Frameworks
NHPI	*N*-hydroxyphthalimide
OFET	Organic Field Effect Transistor
ORR	Oxygen reduction reaction
OTMS	Octadecyltrimethoxysilane
Pcs	Phthalocyanines
PDIs	Perilendiimides
POCs	Porous Organic Cages
POSS	Silsesquioxanes
PVP	Polyvinylpyrrolidone
PXRD	Powder X-ray Diffractiondiffraction
QPPTC	quinoxalinoQuinoxalino[2′,3′:9,10]phenanthro[4,5-abc]phenazine-6,7,15,16-tetracarbonitrile
ROS	Reactive Oxygen Species
SBUs	Secondary Building Units
SCSC	Single crystal to single crystal
SCXRD	Single- Crystal X-ray Diffraction
SPB	Spiroborate
TA	Terephthalaldehyde
TCB	1,2,4-trichlorobenzene
TCNE	Tetracyanoethylene
$TEABF_4$	Tetraethylammonium Tetrafluoroborate
TFB	1,3,5-triformylbenzene
THF	Tetrahydrofuran
UV–vis	Ultraviolet–visible
VOCs	Volatile organic compounds

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