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Efficient Room-Temperature Phosphorescence of a Solid-State Supramolecule Enhanced by Cucurbit[6]uril

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Angew. Chem., Int. Ed., 2019, **58** , 6028 -6032

Azhar
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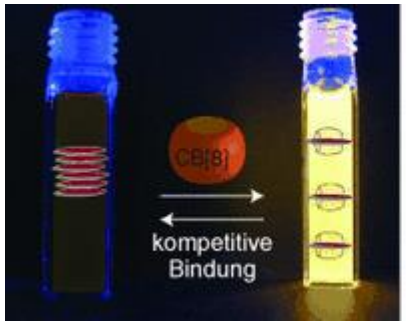
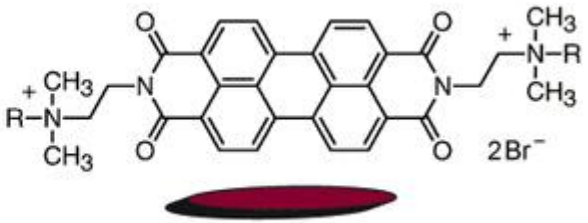
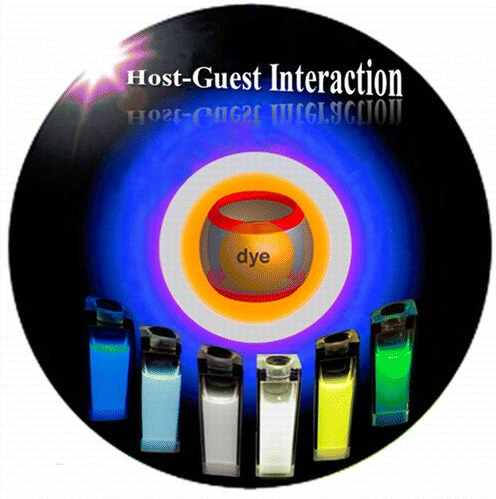
Background Work

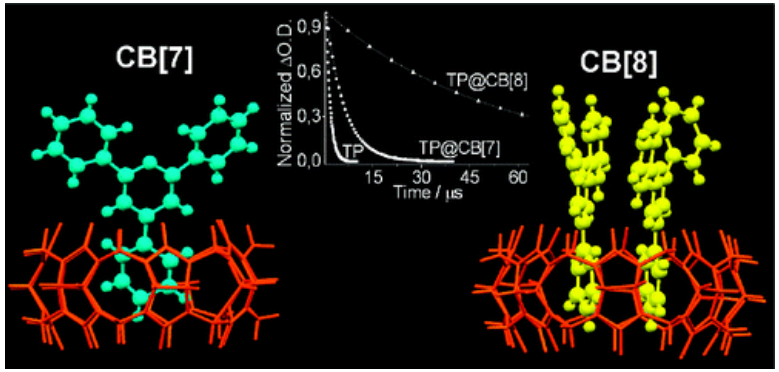




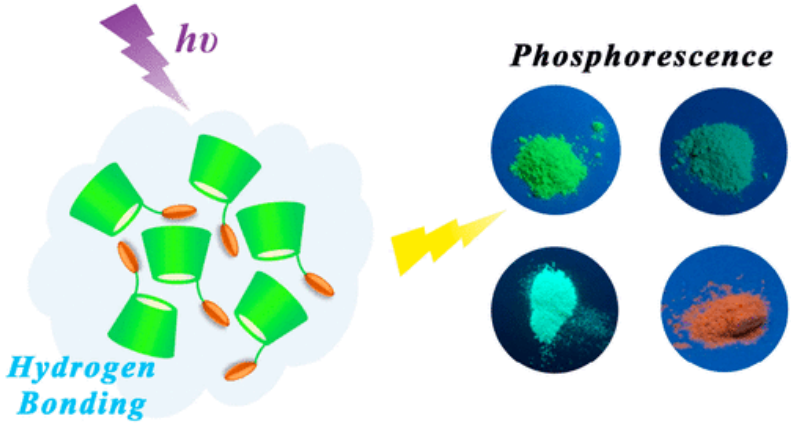
Strongly Fluorescent, Switchable Perylene Bis(diimide) Host–Guest Complexes with Cucurbit[8]uril In Water.
Angew. Chem. Int. Ed. 2012, **51**, 7739 –7743



Facile Cucurbit[8]uril-Based Supramolecular Approach To Fabricate Tunable Luminescent Materials in Aqueous Solution.
J. Am. Chem. Soc. 2016, **138**, 6177-6183

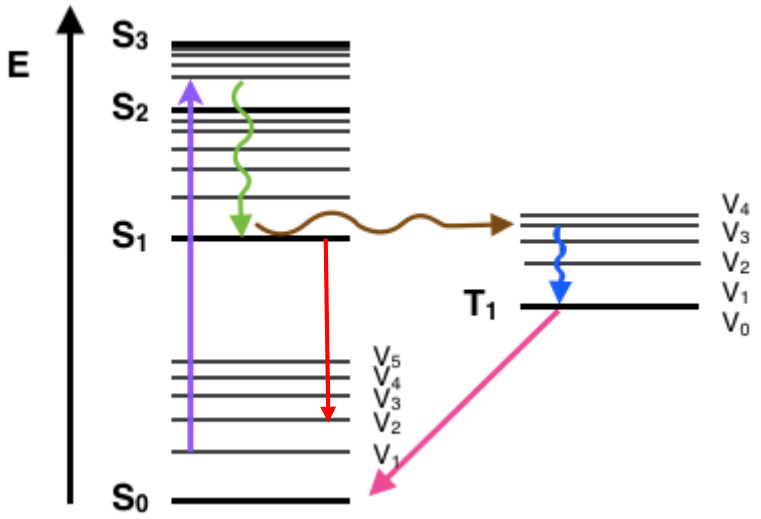


Cucurbituril Complexation Enhances Intersystem Crossing and Triplet Lifetime of 2,4,6-Triphenylpyrylium Ion
J. Phys. Chem. C 2010, **45**, 2034-2038



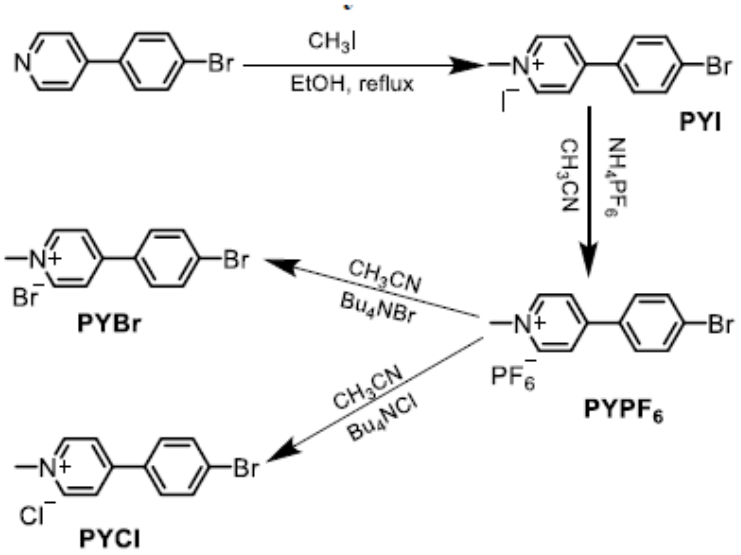
Amorphous Metal-Free Room-Temperature Phosphorescent Small Molecules with Multicolor Photoluminescence via a Host–Guest and Dual-Emission Strategy
*J. Am. Chem. Soc.*2018, **05**, 1916-1923

Jablonski diagram: In molecular spectroscopy, a Jablonski diagram is a diagram that illustrates the electronic states of a molecule and the transitions between them. The states are arranged vertically by energy and grouped horizontally by spin multiplicity.



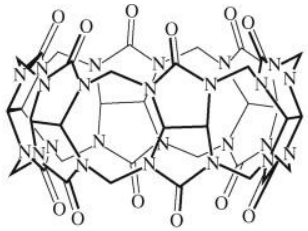
Possible scenario with absorption, internal conversion, vibrational relaxation, fluorescence, intersystem crossing, and phosphorescence processes shown.

Transition	Time Scale
Internal Conversion	10^{-14} - 10^{-11} s
Vibrational Relaxation	10^{-14} - 10^{-11} s
Absorption	10^{-15} s
Phosphorescence	10^{-4} - 10^{-1} s
Intersystem Crossing	10^{-8} - 10^{-3} s
Fluorescence	10^{-9} - 10^{-7} s



Synthesis of bromophenyl-methyl-pyridinium halide (PYX)

Cucurbiturils are macrocyclic molecules made of glycoluril (=$C_4H_2N_4O_2$=) monomers linked by methylene bridges (-CH_2-). The oxygen atoms are located along the edges of the band and are tilted inwards, forming a partly enclosed cavity.



cucurbit[6]uril

Why this paper?

Room-temperature phosphorescent (RTP) has got tremendous attention due to their extensive application such as organic light-emitting diodes, bioimaging, information storage and encryption and so on.

However, achieving ultralong RTP (generally from seconds to hours) is extremely difficult due to two main issues:

i) The intrinsically weak spin–orbit coupling of molecules makes it hard to achieve efficient intersystem crossing (ISC);

ii) a long triplet state (T_1) lifetime means that T_1 will suffer tremendously from quenching.

To achieve efficient RTP, new methods have been developed such as special design of structure, embedding into proper matrix, crystallization and so on.

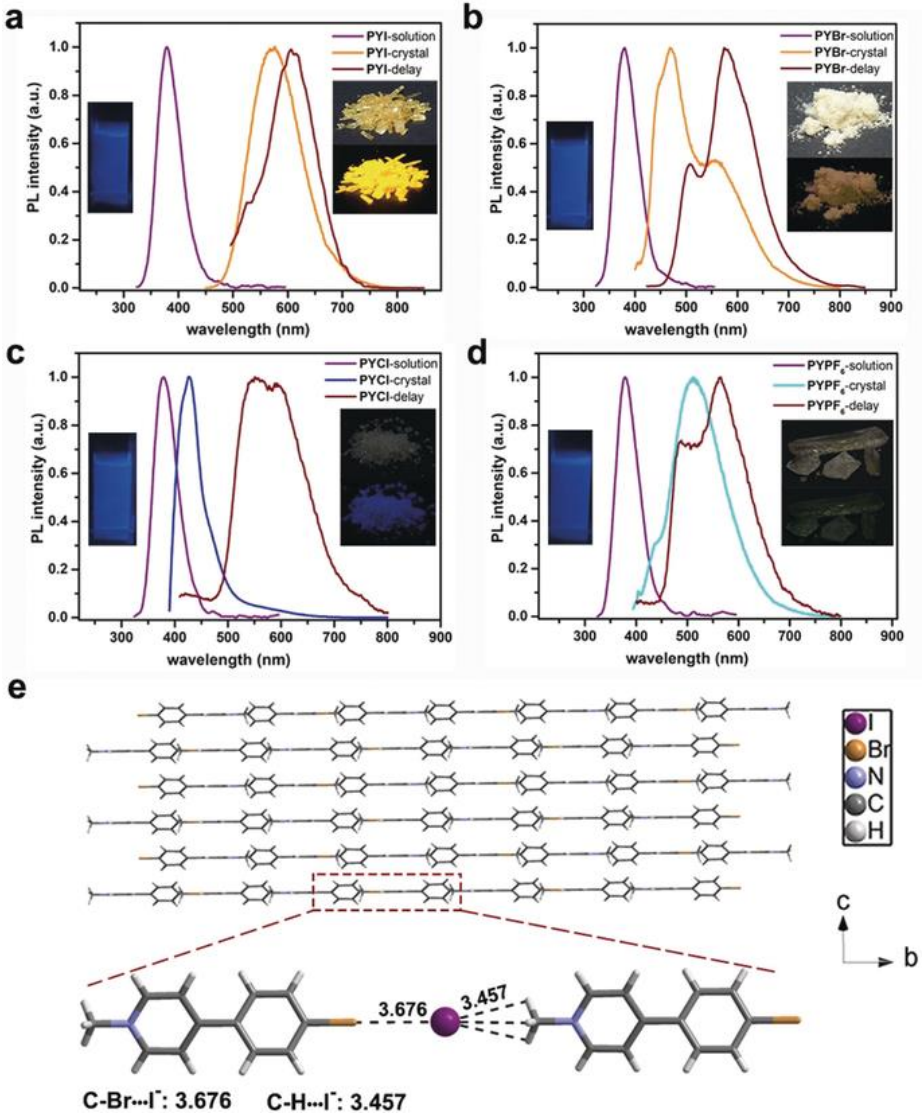
In this paper...

Supramolecular approach has been used to construct functional materials by complexing or assembly to enhance the efficiency and extend the lifetime of phosphorescence.

Noncovalent interactions, such as host-guest interaction alter the properties of guests greatly.

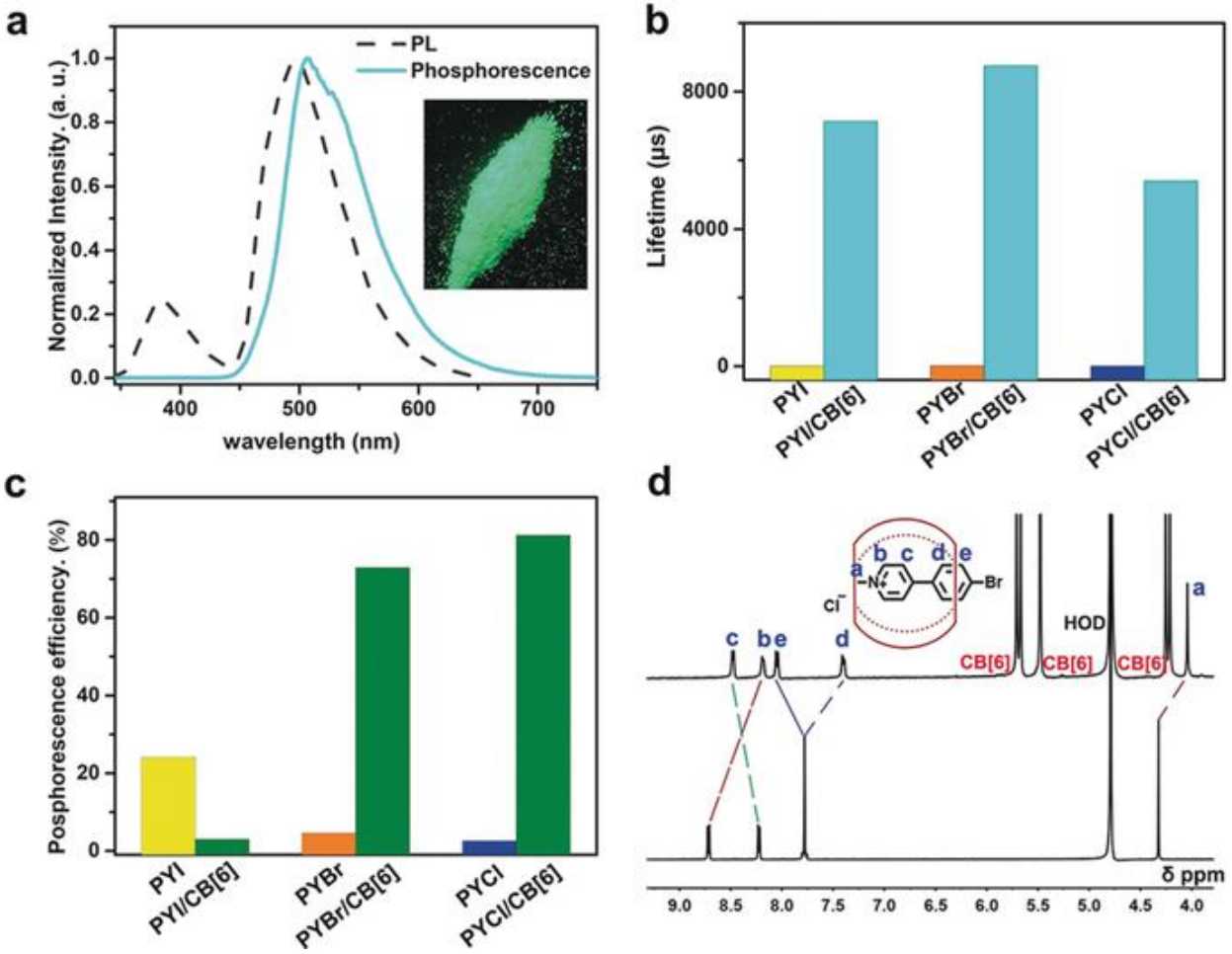
Reported an uncommon enhancement of phosphorescence quantum yield of bromophenyl-methyl-pyridinium chloride (PYCl) from 2.6% to 81.2% by complexing with cucurbit[6]uril (CB6), which is the highest phosphorescence quantum yield of purely organic systems so far.

Results and discussion



a) Photoluminescence spectra of PYI in solid (orange line), solution (violet line) and phosphorescence spectra (wine line); b) Photoluminescence spectra of PYBr in solid (orange line), solution (violet line) and phosphorescence spectra (wine line); c) Photoluminescence spectra of PYCl in solid (blue line), solution (violet line) and phosphorescence spectra (wine line); d) Photoluminescence spectra of PYPF6 in solid (cyan line), solution (violet line) and phosphorescence spectra (wine line) (inset: left, pictures of PYX in solution under 304 nm lamp; right, PYX crystal under ambient light and 365 nm lamp); e) Single-crystal X-ray diffraction analysis of PYI.

Results and discussion



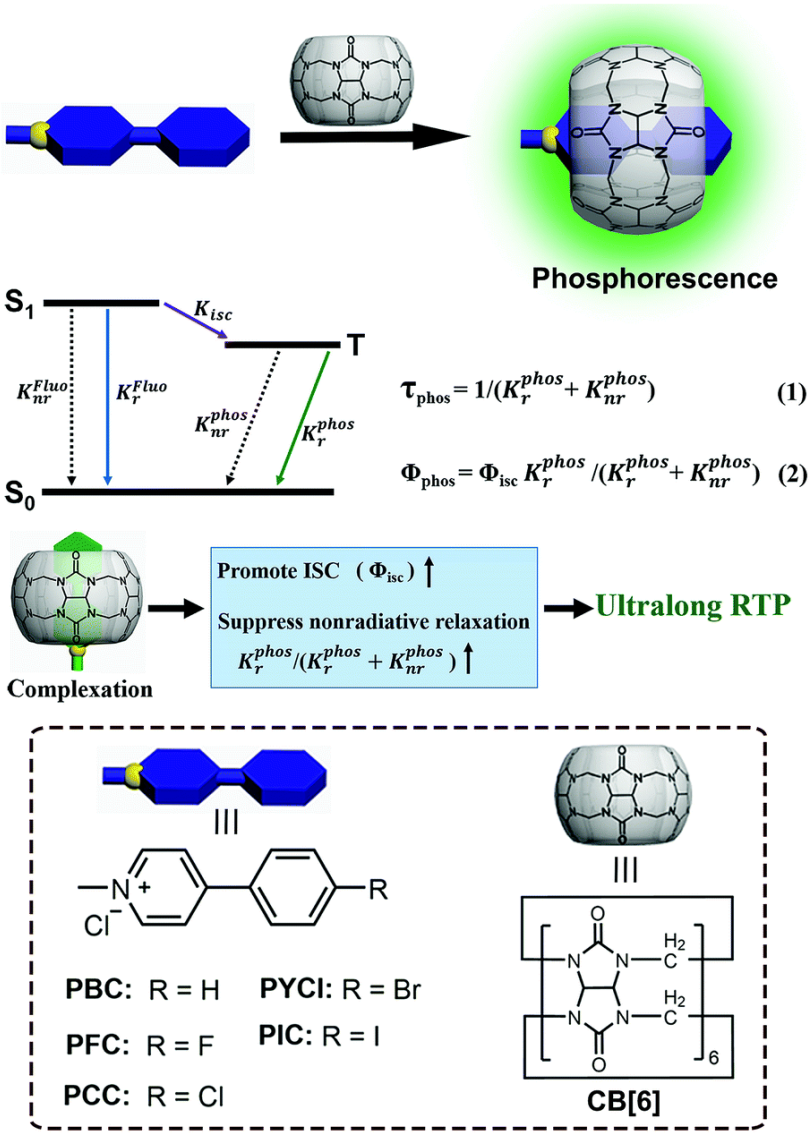
Photophysical properties of PYCl and PYCl/CB[6] in solid under ambient conditions. a) Steady-state photoluminescence (PL, gray dashed line) and phosphorescence (cyan solid line) spectra of PYCl/CB[6] complex under 334 nm excitation (inset: photograph of PYCl/CB[6] under 365 nm); b) Lifetime of PYX and PYX/CB[6]; c) Phosphorescence quantum efficiency of PYX and PYX/CB[6]; d) 1H NMR spectra of PYCl/CB[6] and PYCl.

Results and discussion

Samples	λ_{ex} (nm)	λ_{Phos} (nm)	τ_p (μs)	Φ_P (%)
PYI	386	575	5.61	24.1
PYBr	398	470	6.66	4.6
PYCl	381	426	5.76	2.6
$PYPF_6$	382	510	5.66	0.4
PYCl/CB[6]	360	500	5400	81.2
PYBr/CB[6]	360	500	8748	72.9
PYI/CB[6]	361	500	7135	3.0
PYCl+ CB[5]	304	411	8.52	3.2
PYCl+ CB[7]	307	482	2200	3.3

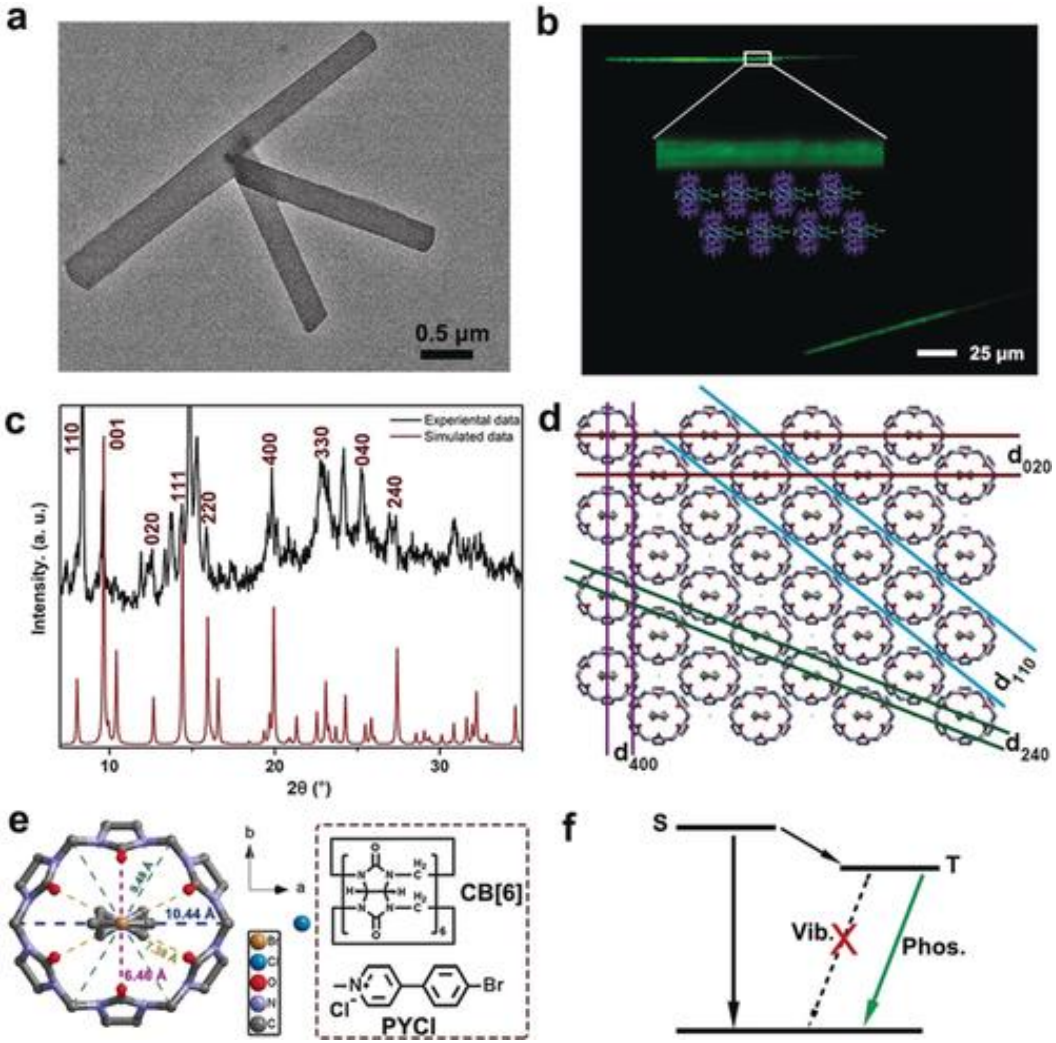
Photophysical data of PYX and PYX+CB.

Results and discussion



Schematic illustration of the solid-state supramolecular strategy and Jablonski

Results and discussion



a) TEM image of PYCl/CB[6]; b) LSCM image of PYCl/CB[6] (inset: the cartoon of linear array); c) XRD patterns of PYCl/CB[6] (black line: experimental data; red line: simulated data based on crystal); d) Schematic illustration of planes based on XRD; e) Crystal structure of PYCl/CB[6] view in c-axis and their chemical structure; f) The efficient phosphorescence emission of PYCl/CB[6].

Conclusions

Novel fibrous supramolecular assembly has been constructed by chromophore PYCl and CB[6] which shows up to 81.2% phosphorescence quantum yield.

PY with different counterions exhibits various quantum efficiency from 0.4% to 24.1%.

The complexion of CB[6] promotes phosphorescence quantum efficiency by encapsulation which suppresses the nonradiative decay and promotes the ISC.

Enhancement for phosphorescence is particular for CB[6], larger or smaller host display no such facilitation.