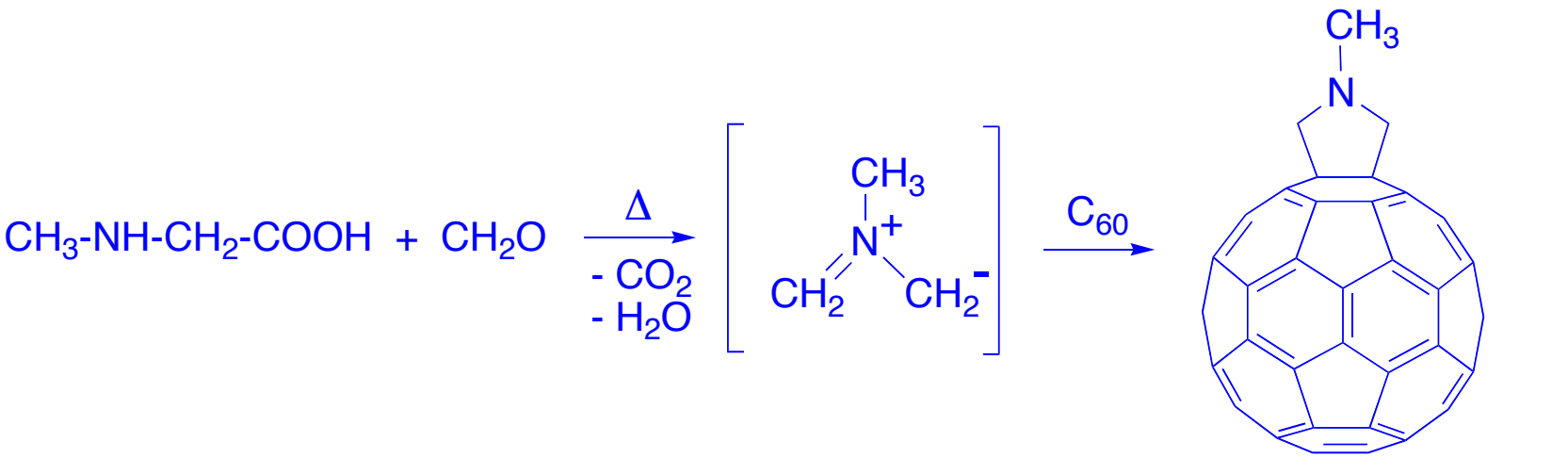
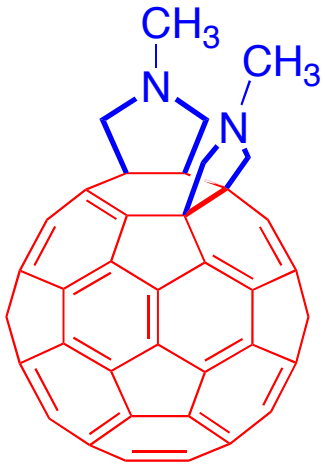
Azomethine Ylide Cycloaddition to C_{60}

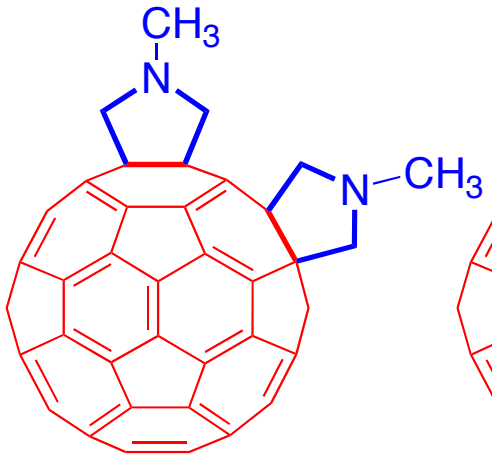


(41 % yield, 82 % based on C_{60} recovery)

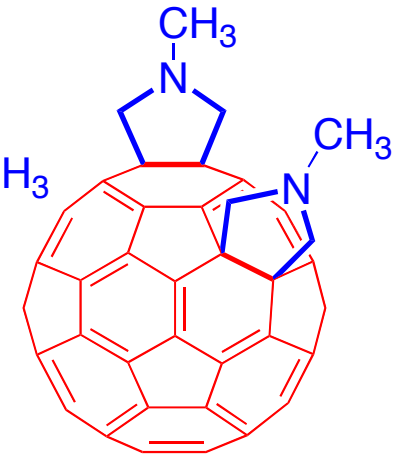
Maggini, Scorrano, Prato *JACS* **1993** *115* 9798



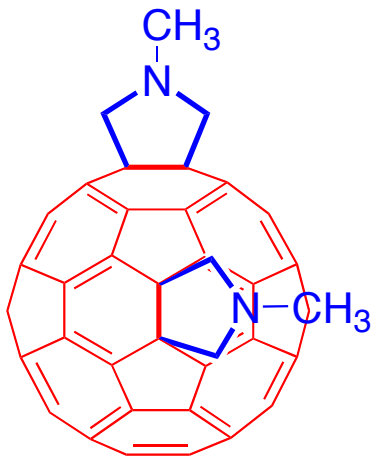
cis-1



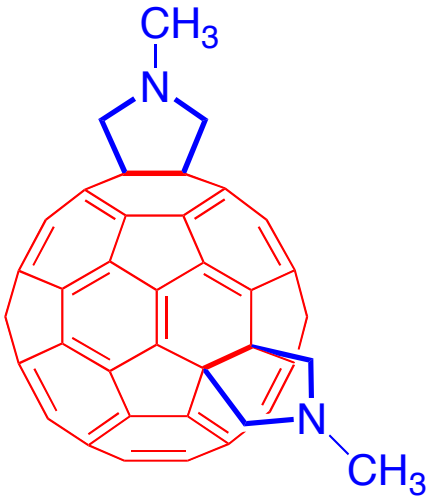
cis-2



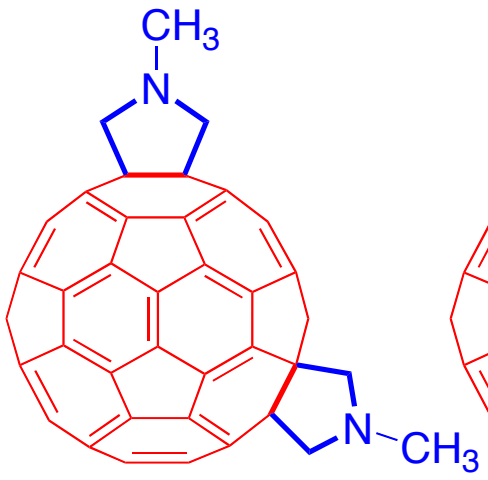
cis-3



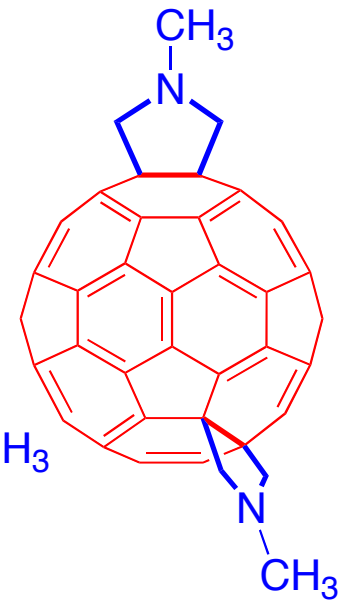
equatorial



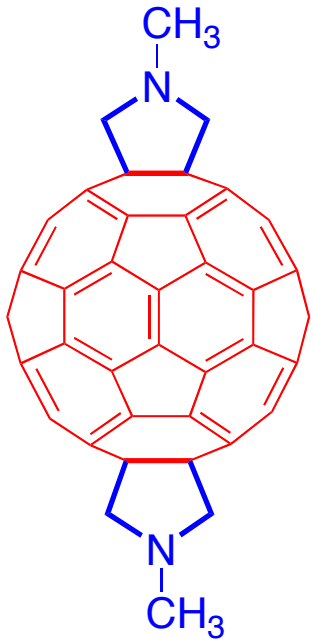
trans-4



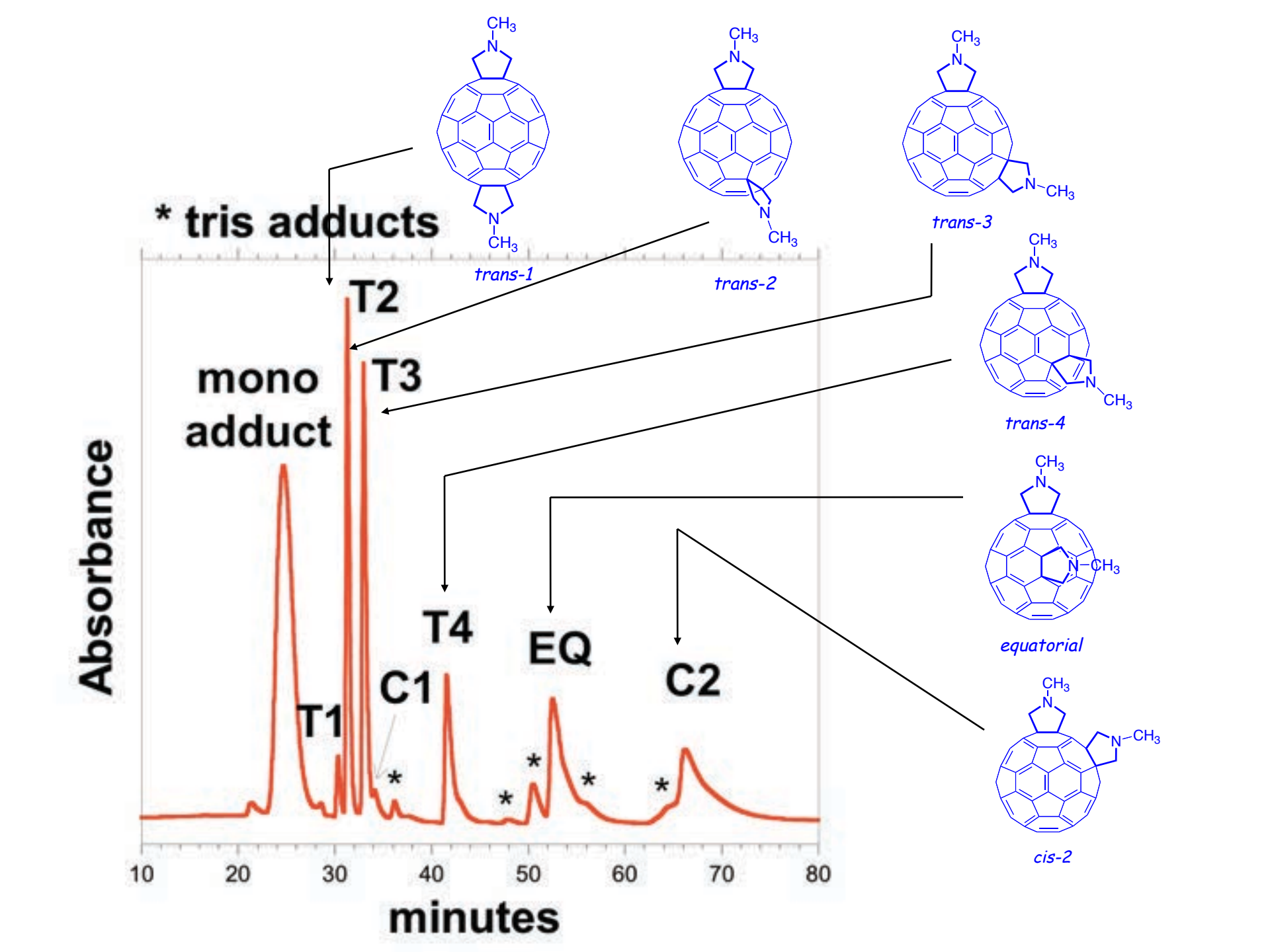
trans-3



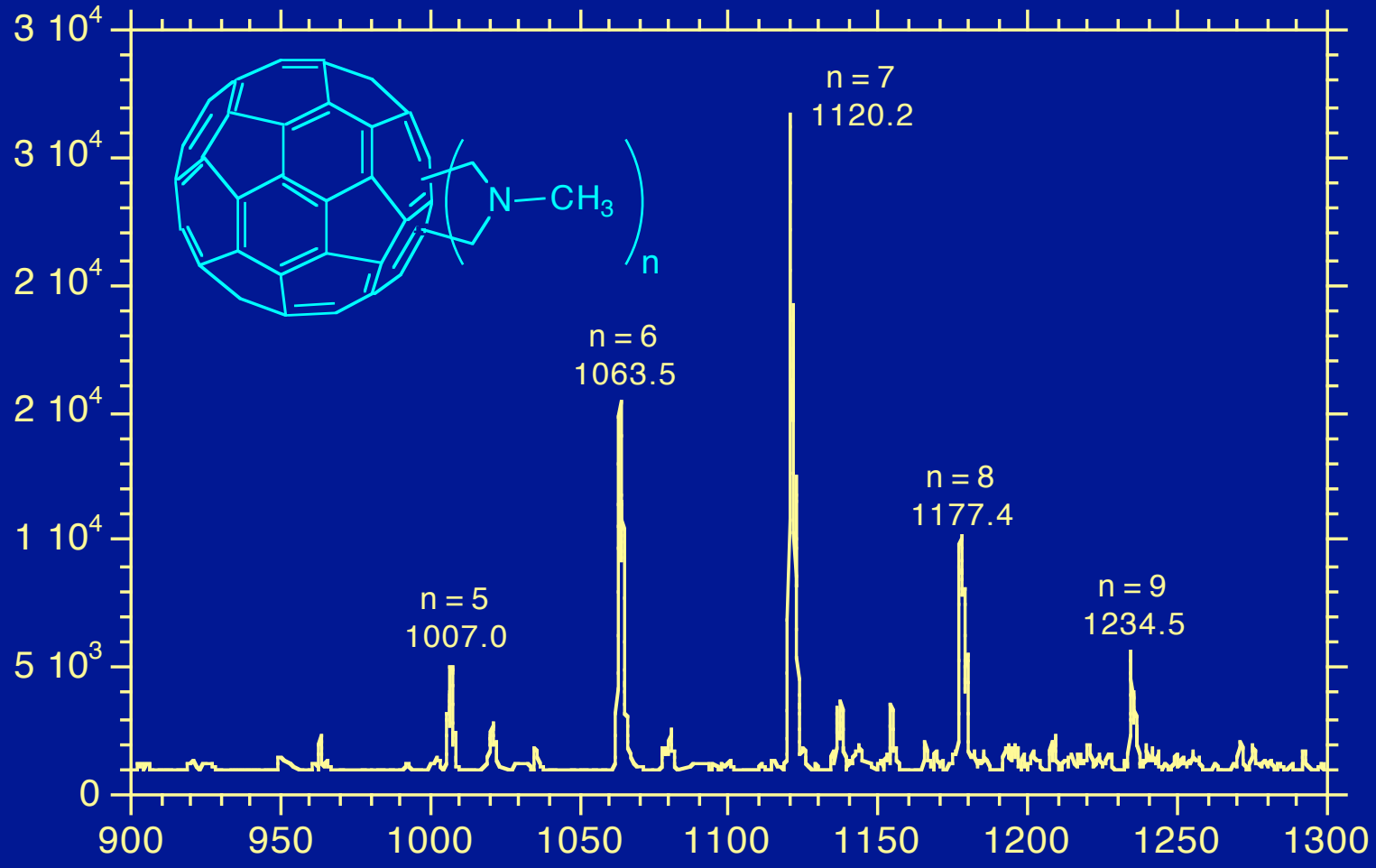
trans-2



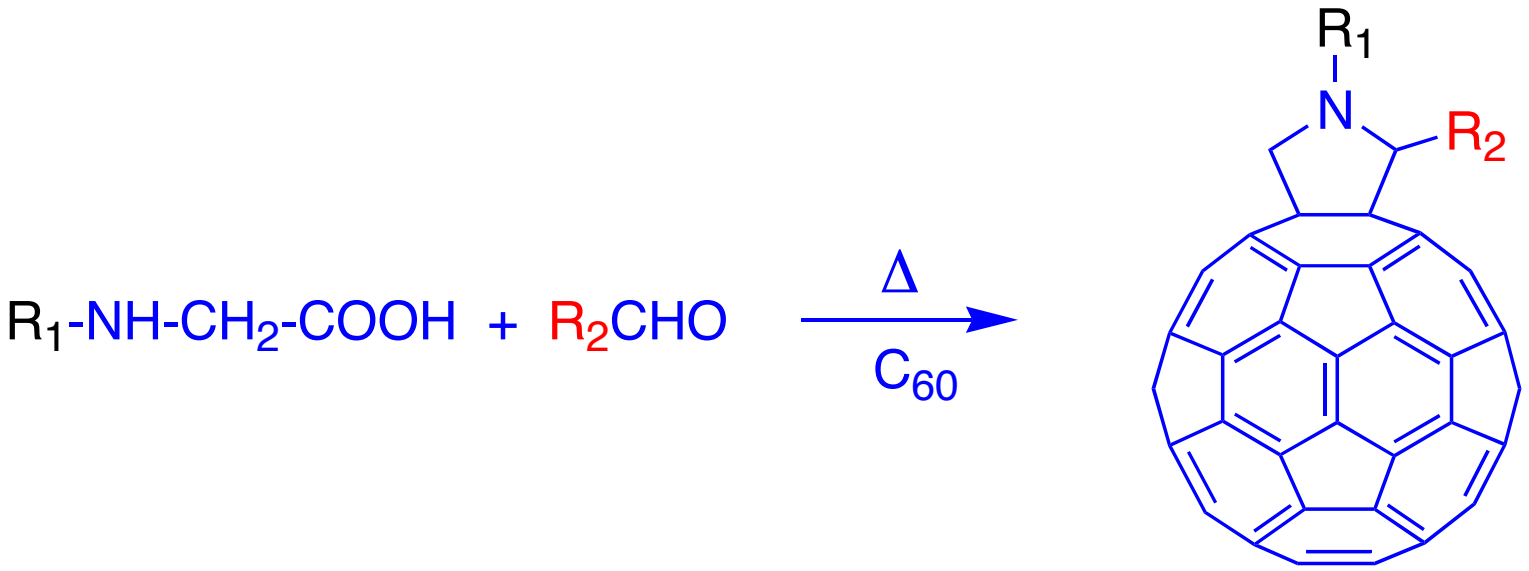
trans-1


* tris adducts
mono adduct
T1
T2
T3
T4
C1
EQ
C2
Absorbance
minutes
10
20
30
40
50
60
70
80
trans-1
trans-2
trans-3
trans-4
equatorial
cis-2

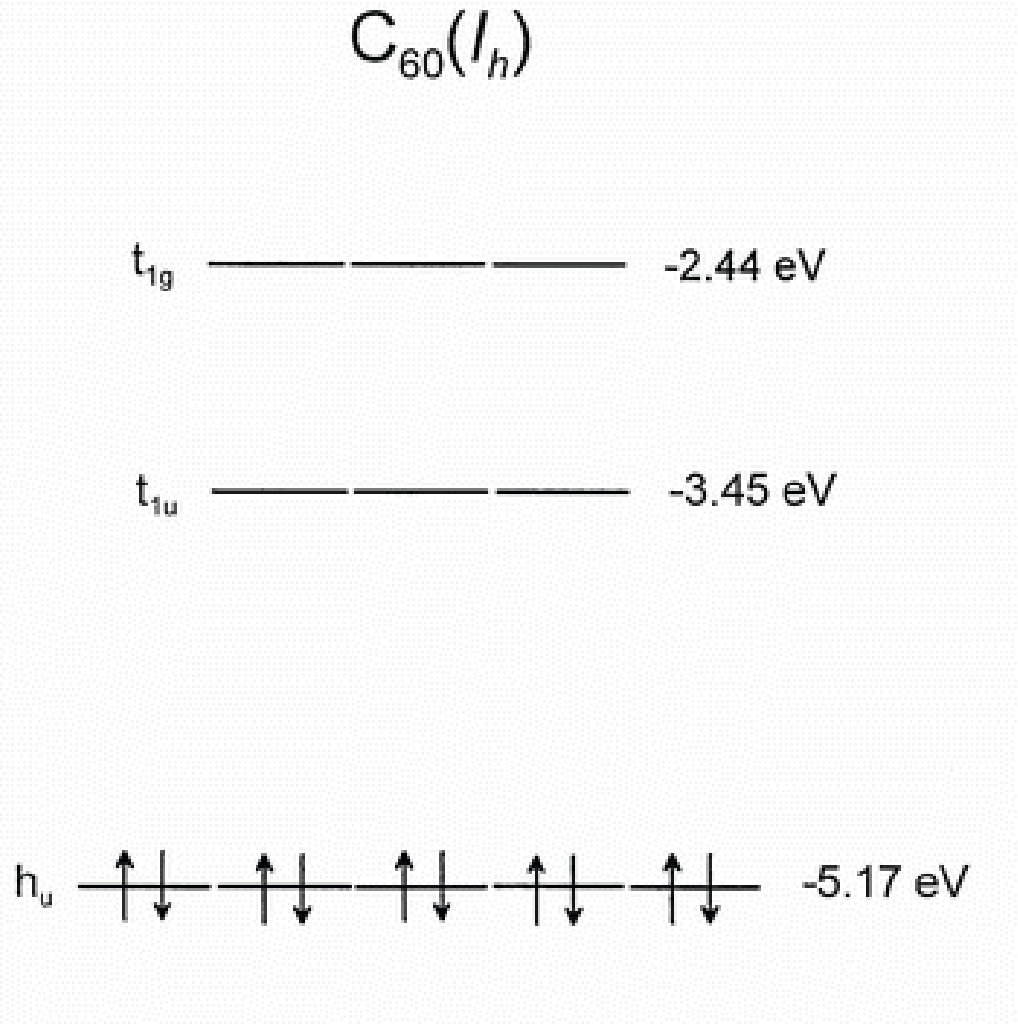
CH_3-NH-CH_2-COOH (20 eq) + HCHO (20 eq) + C_{60} $\xrightarrow[8h]{\text{toluene, }\Delta}$



General Approach to Functionalized Fulleropyrrolidines

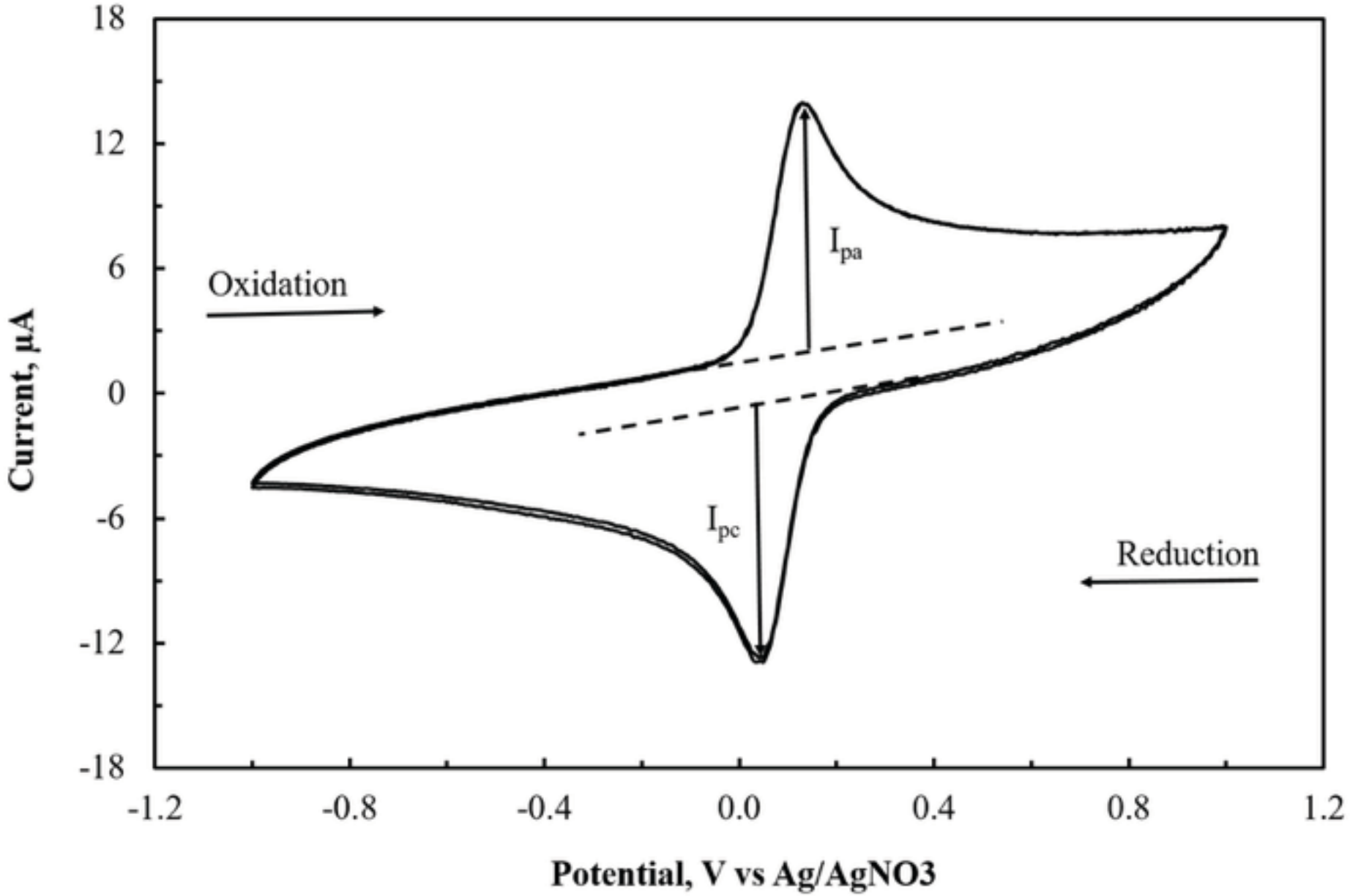


Maggini, Scorrano and Prato, *JACS*, **1993**, *115*, 9798
Prato and Maggini, *Acc. Chem. Res.*, **1998**, *31*, 519
Tagmatarchis and Prato, *Synlett* **2003**, *6*, 768

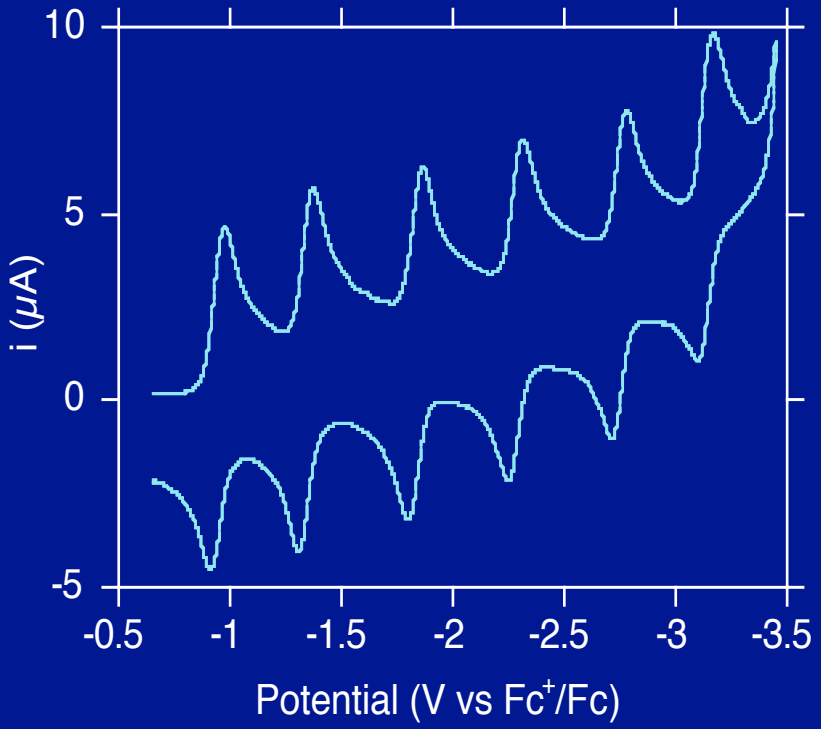


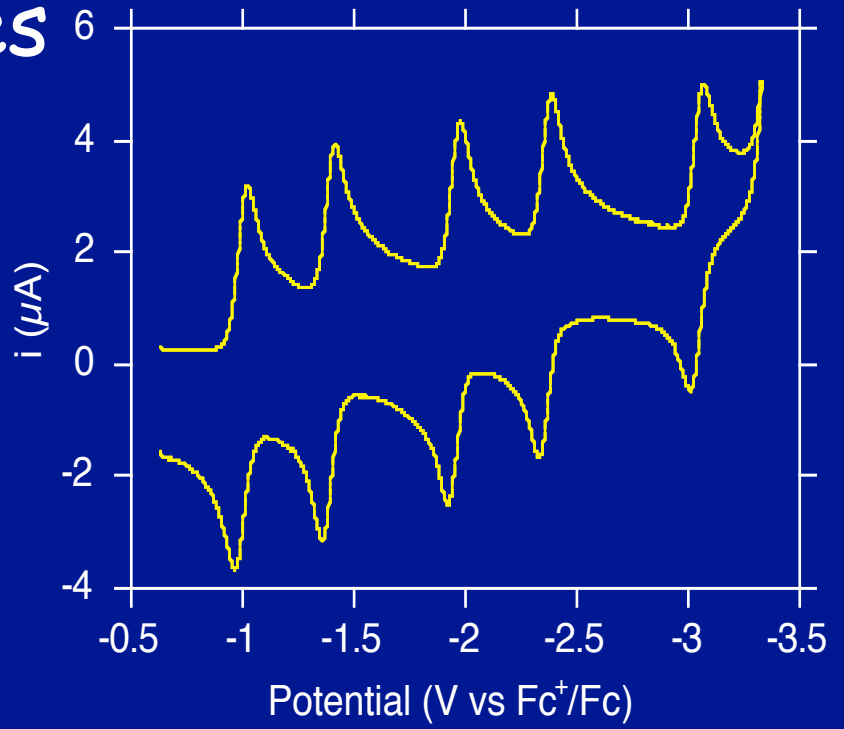
Nature **393**, 668-671(18 June 1998)

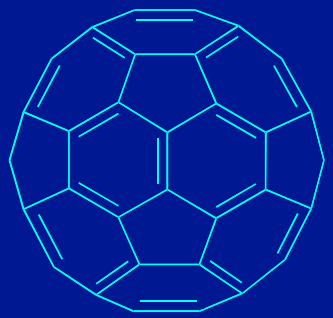
Cyclic Voltammogram of Ferrocene



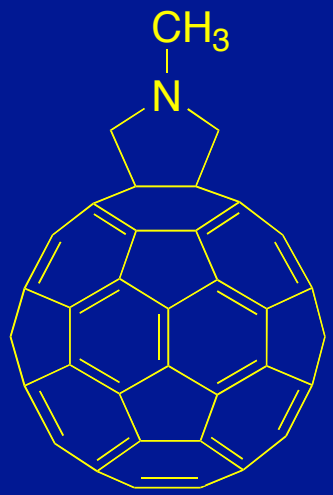
Electrochemical Properties



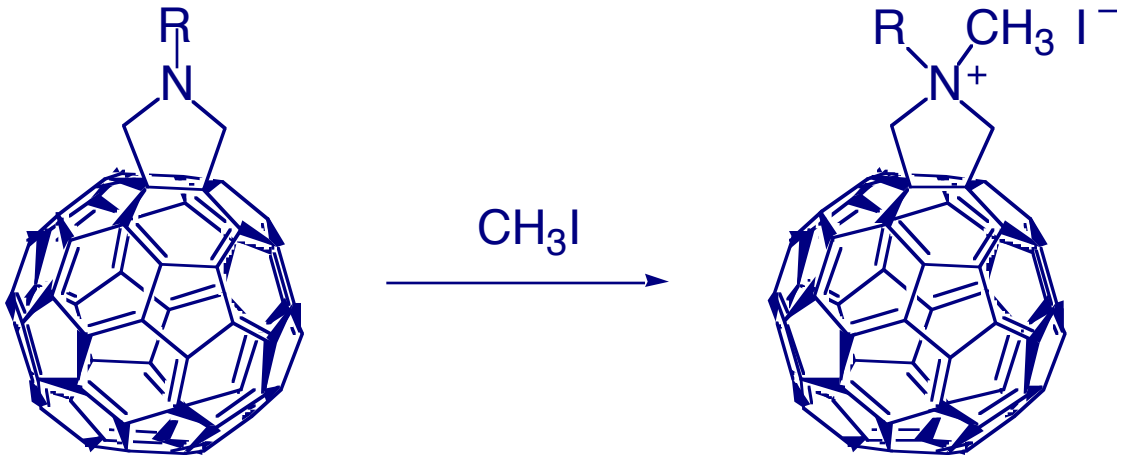




	$E^{0/1-}$	$E^{1-/2-}$	$E^{2-/3-}$	$E^{3-/4-}$	$E^{4-/5-}$	$E^{5-/6-}$
C_{60}	- 0.94	- 1.33	- 1.83	- 2.28	- 2.74	- 3.14
1	- 1.05	- 1.44	- 2.01	- 2.42	- 3.12	

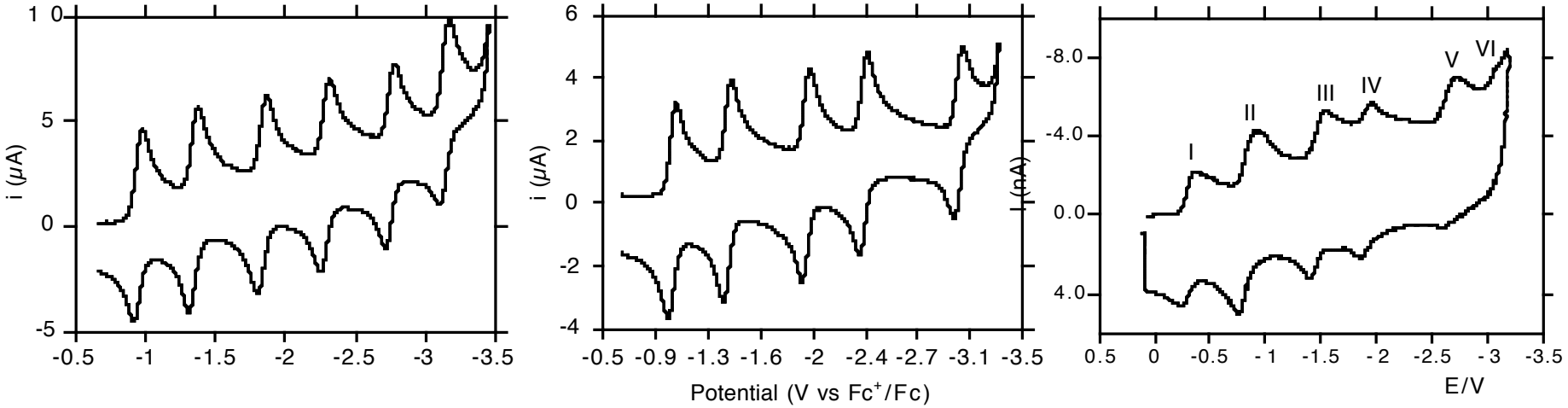


N-Me-Fulleropyrrolidinium Ions are Better Acceptors



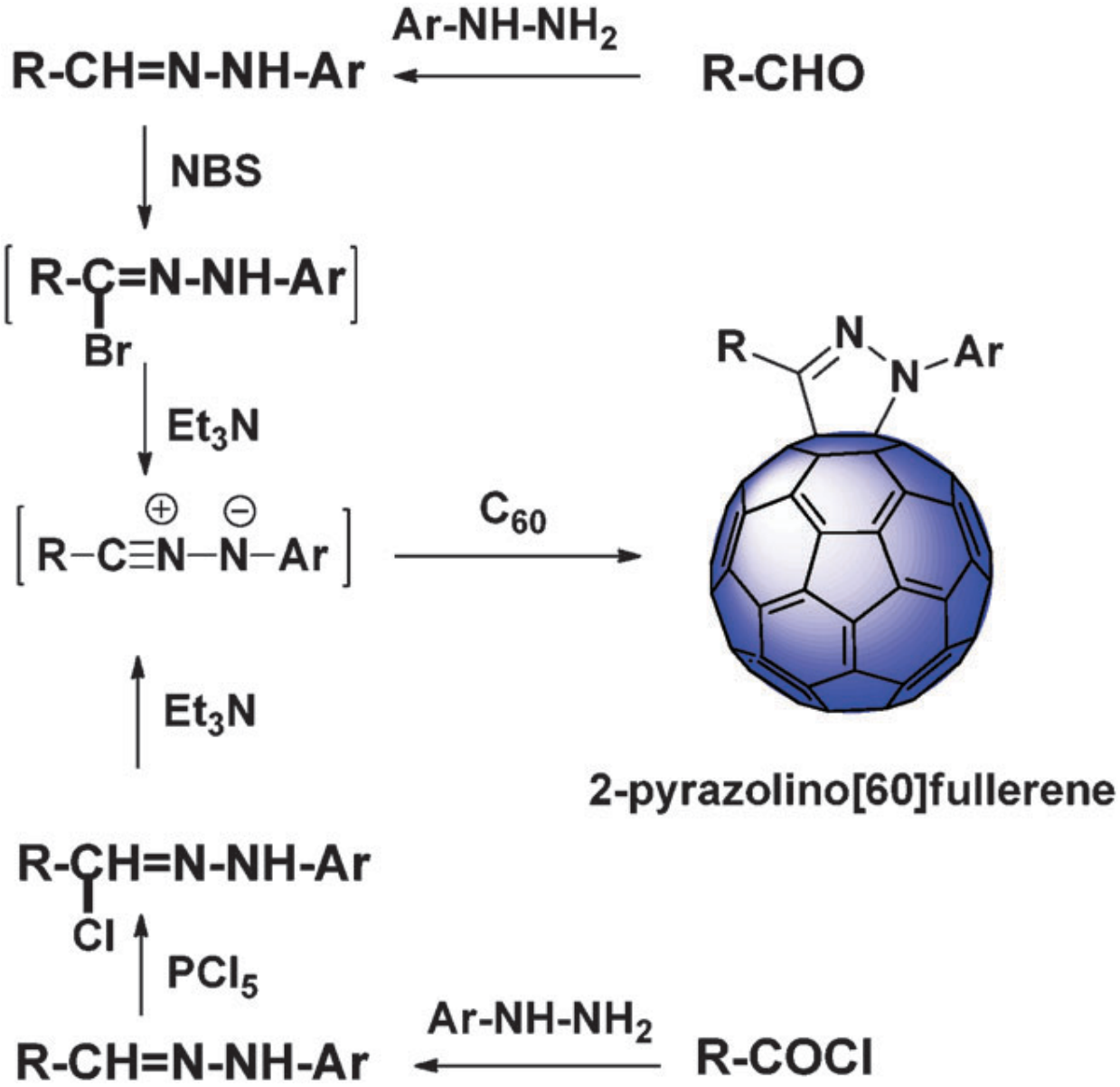
E1/2 values (V vs SCE) -0.47 -0.29

C_{60} -0.35

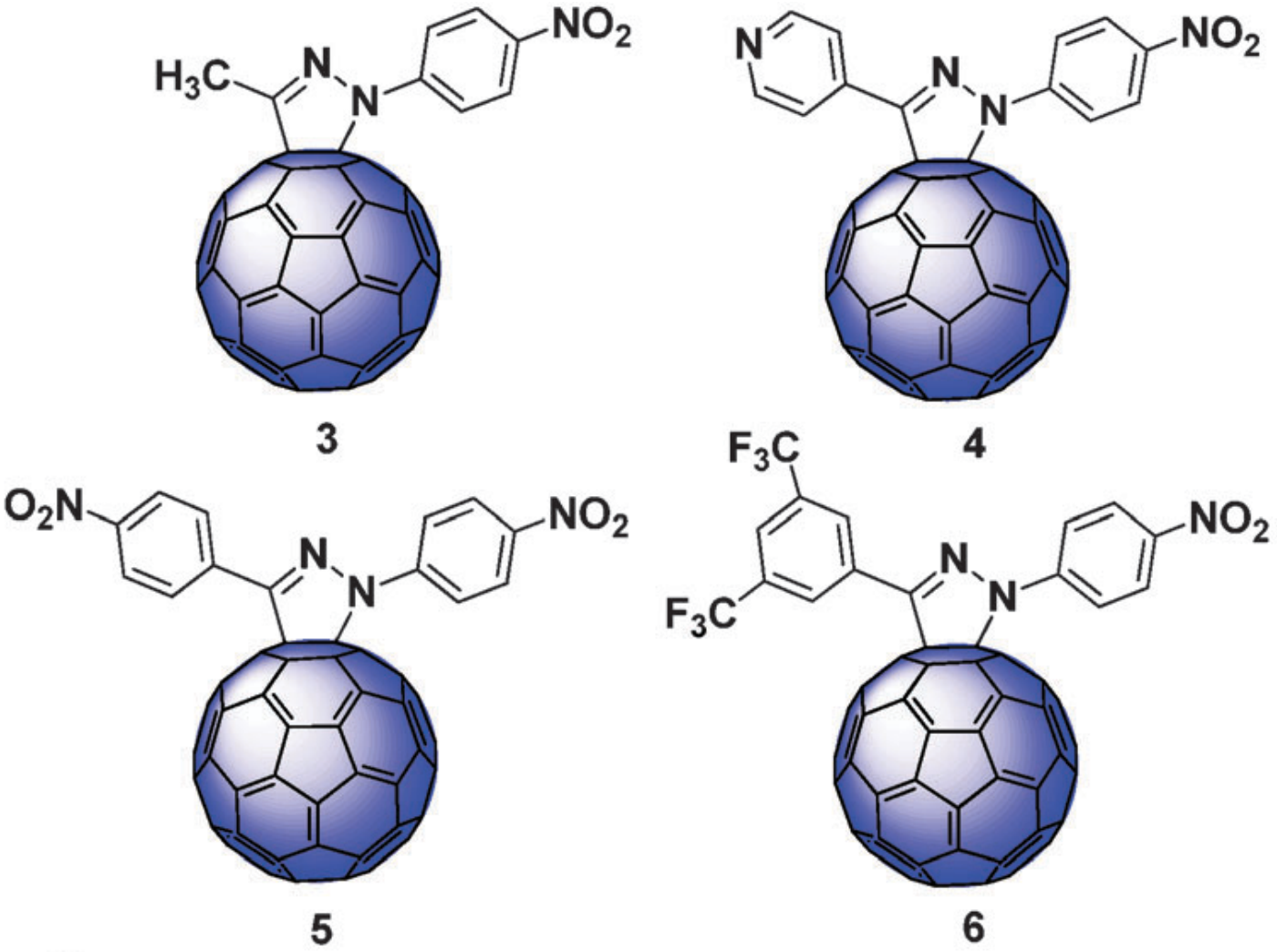


J. Am. Chem. Soc., 1998, 120, 11645

Synthesis of Pyrazolino-Fullerenes



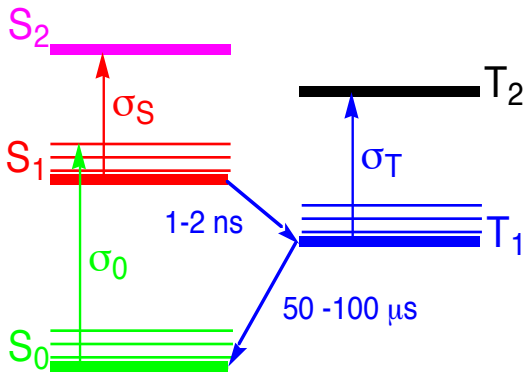
F. Langa *Chem. Soc. Rev.,* 2011, 40, 5232–5241

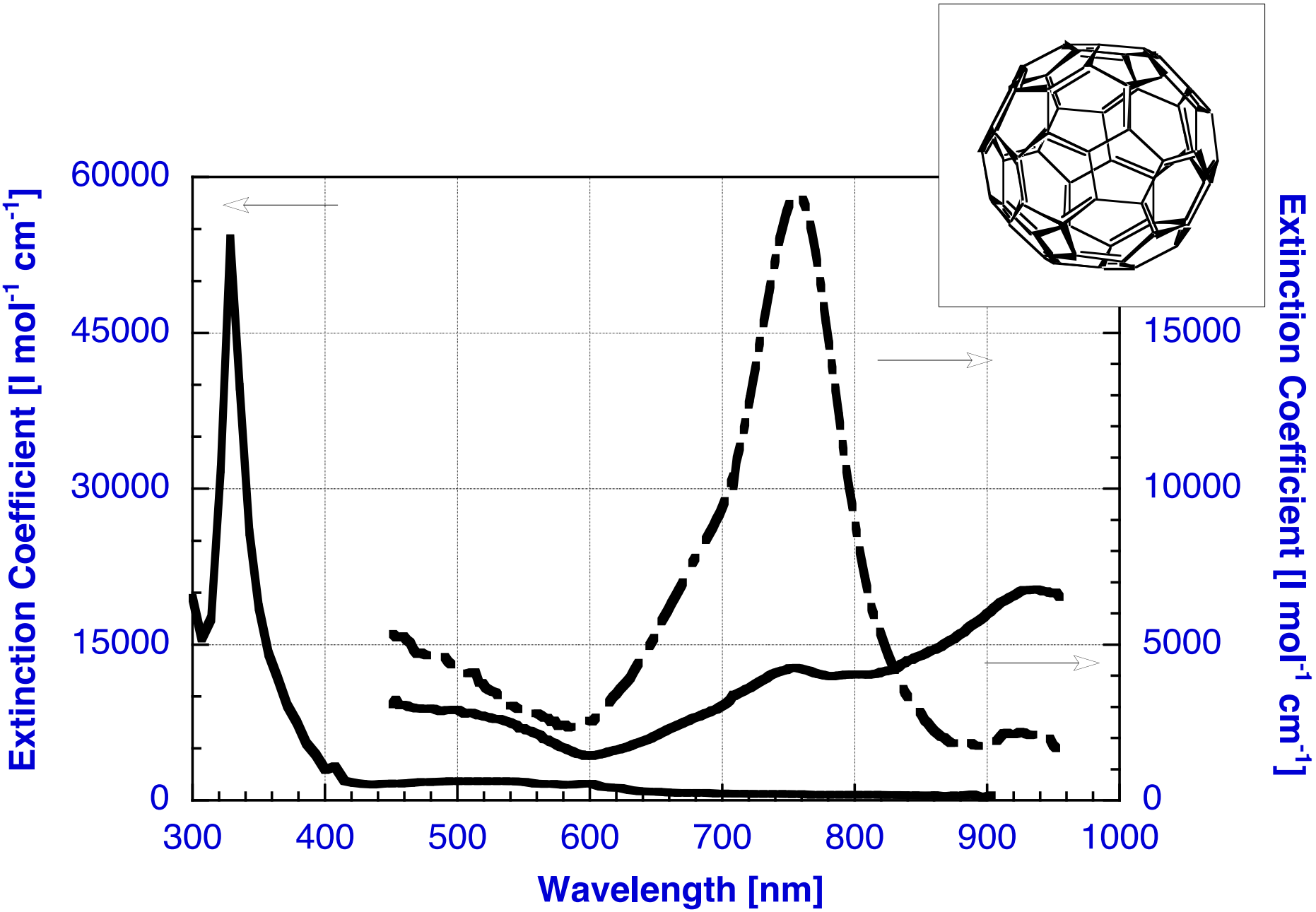


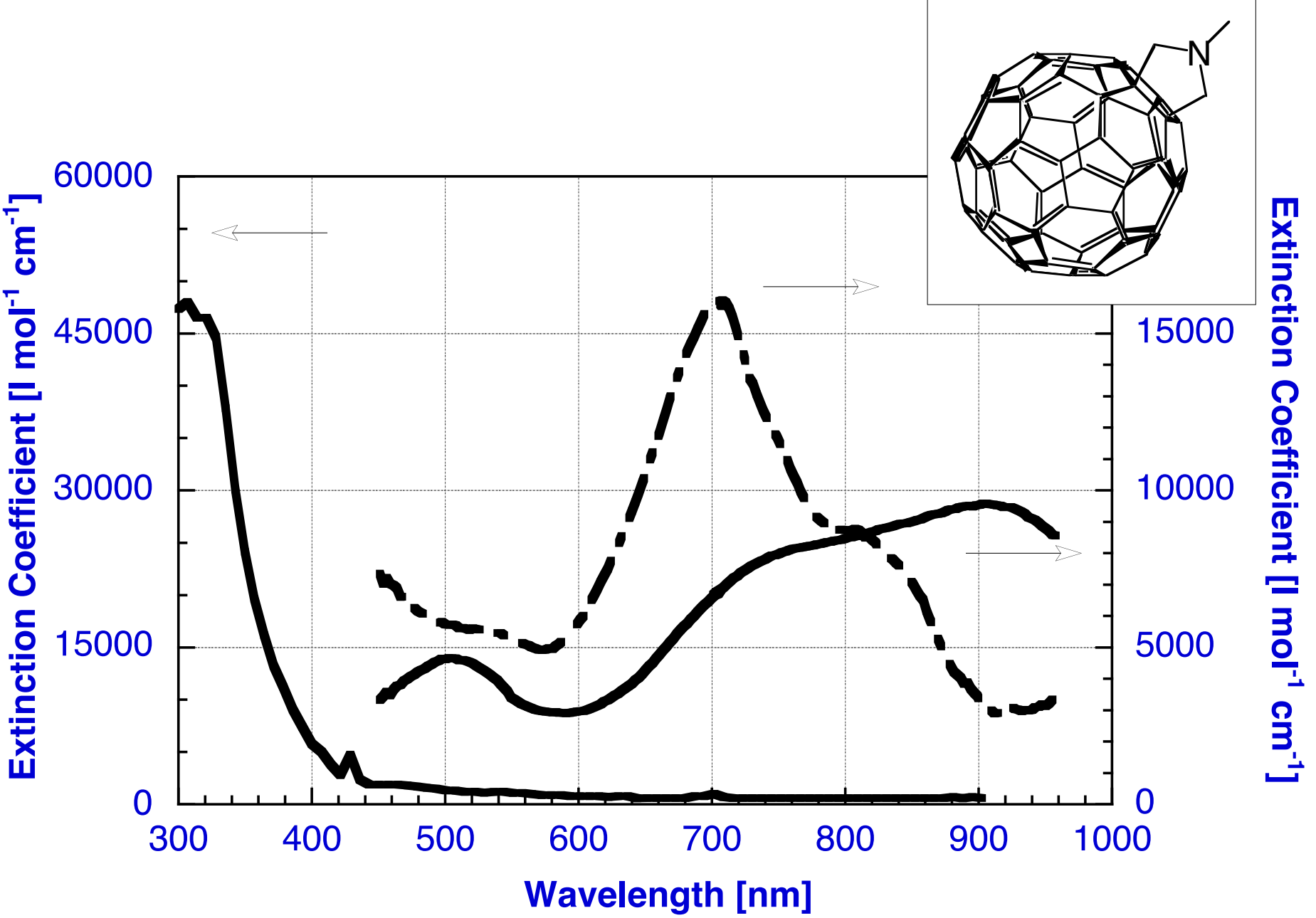
40 mV for **4**, 60 mV for **5** or 70 mV for **6**

F. Langa *Chem. Soc. Rev.,* 2011, 40, 5232–5241

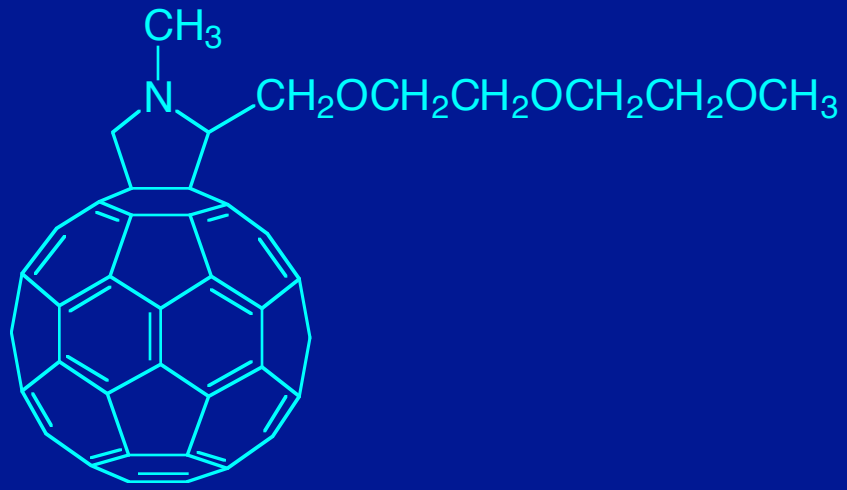
Ground State and First Triplet Excited State Absorptions in Unmodified C_{60}



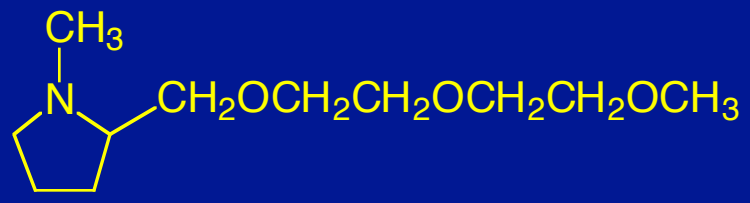

60000
45000
30000
15000
0
Extinction Coefficient [l mol-1 cm-1]
15000
10000
5000
0
Extinction Coefficient [l mol-1 cm-1]
300
400
500
600
700
800
900
1000
Wavelength [nm]


Extinction Coefficient [l mol-1 cm-1]
60000
45000
30000
15000
0
300
400
500
600
700
800
900
1000
Wavelength [nm]
15000
10000
5000
0
Extinction Coefficient [l mol-1 cm-1]
N

Fulleropyrrolidines are much less basic than regular amines



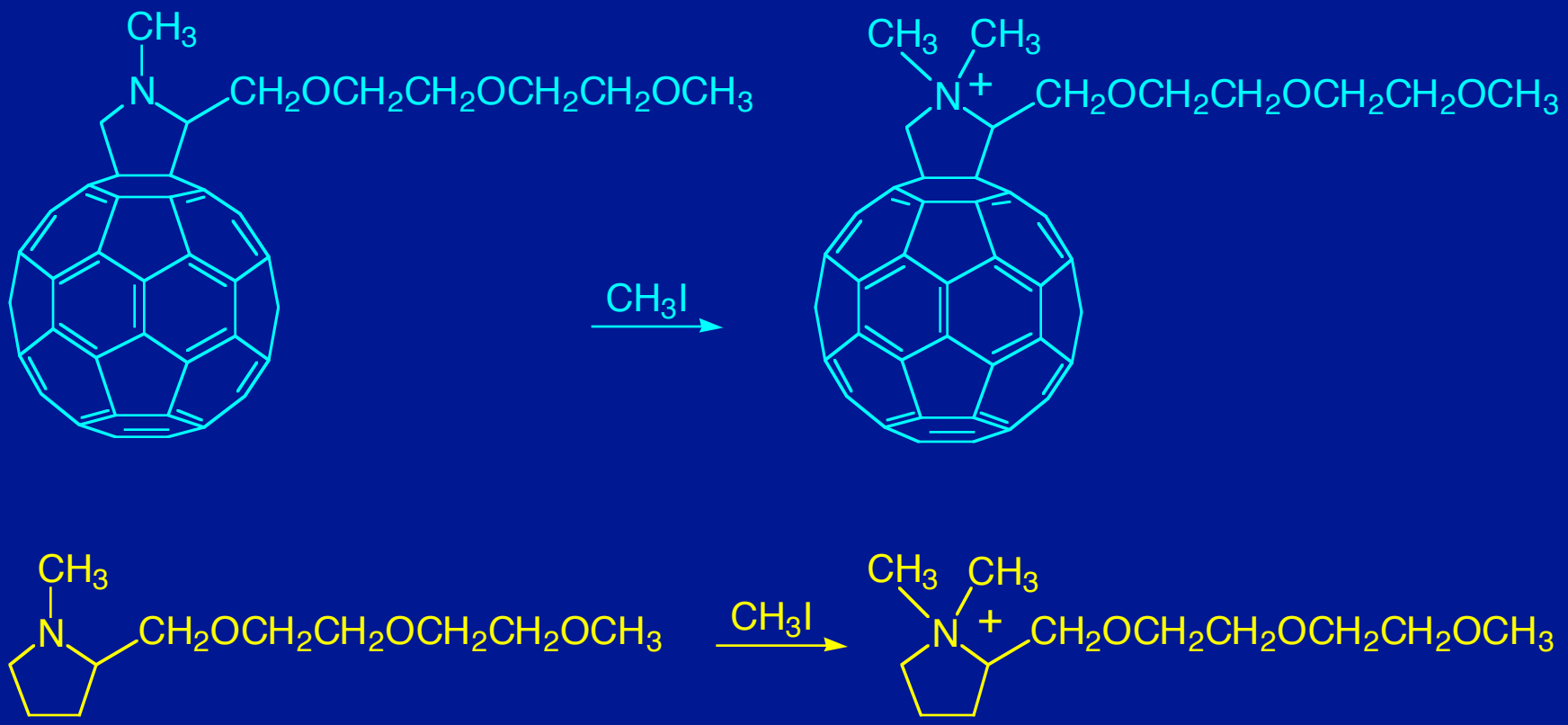
$pK_a = 5.6 \pm 0.01$



$pK_a = 11.1 \pm 0.01$

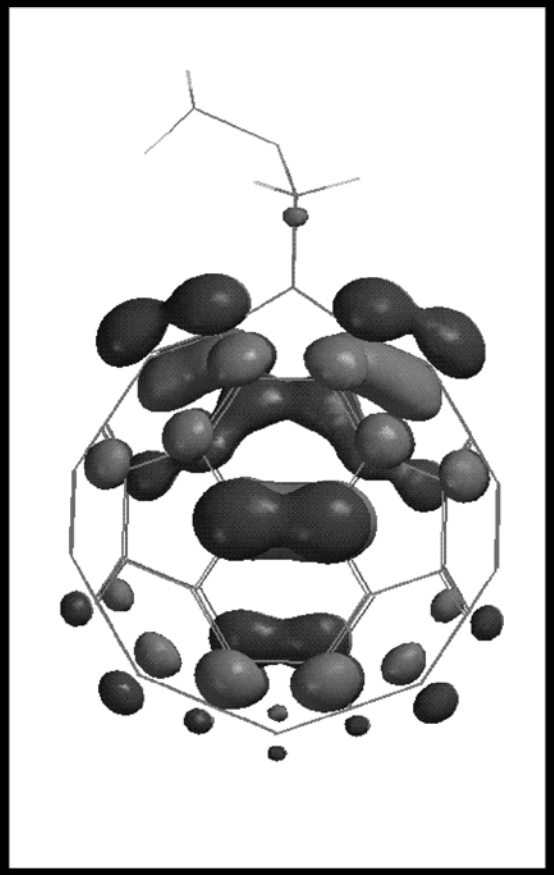
measured in dioxane/water 85/15

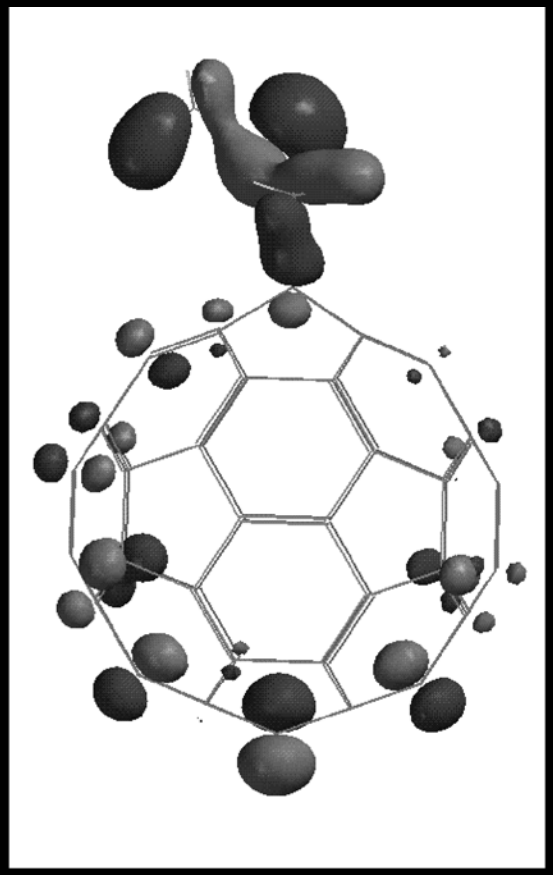
Bagno, A.; Claeson, S.; Maggini, M.; Martini, M. L.; Prato, M.; Scorrano, G. Chem. Eur. J. **2002**, 8, 1016



Pyrrolidine reacts 500 times faster than fulleropyrrolidine

Bagno, A.; Claeson, S.; Maggini, M.; Martini, M. L.; Prato, M.; Scorrano, G. Chem. Eur. J. **2002**, 8, 1016

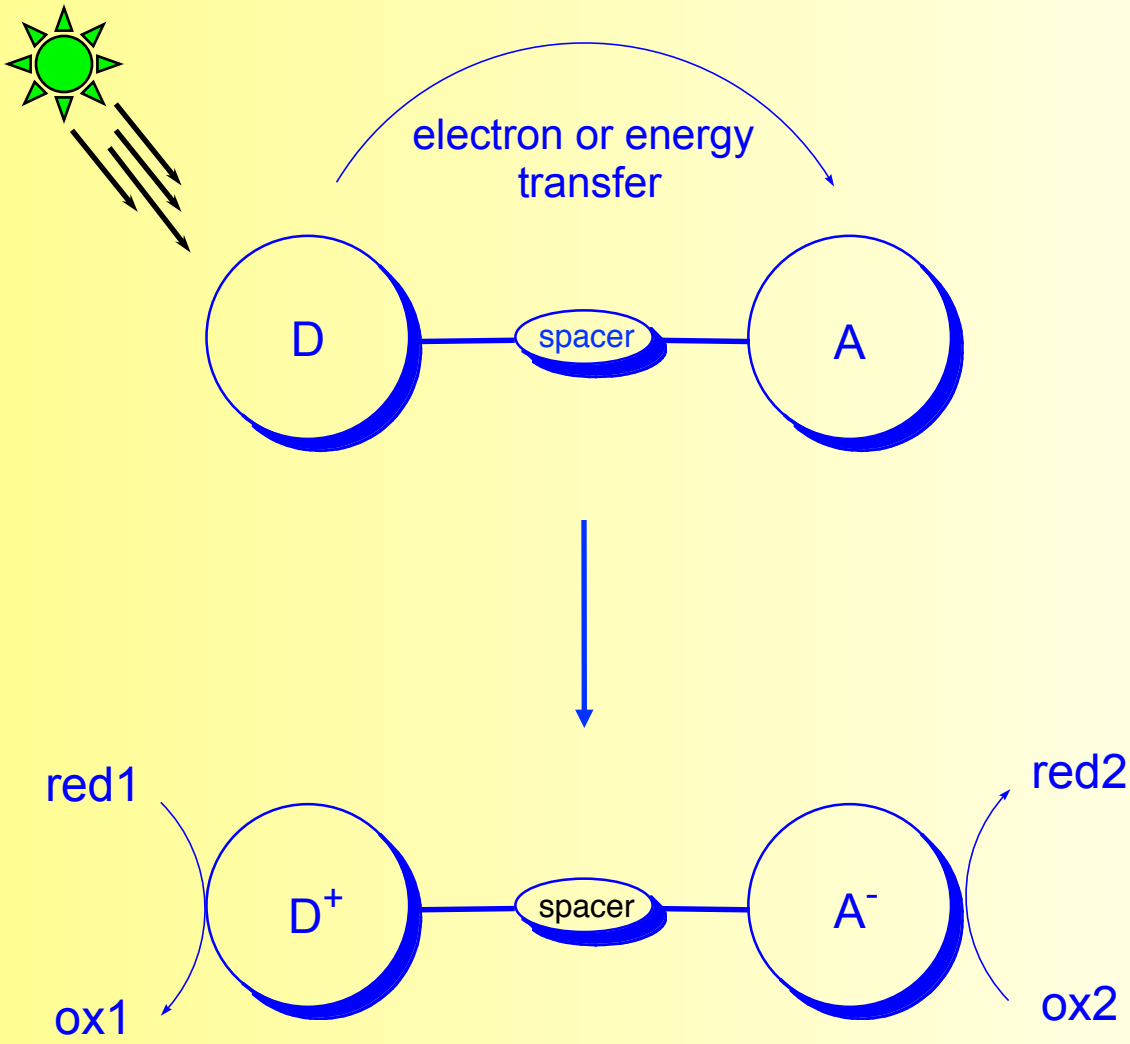




HOMO HOMO -4

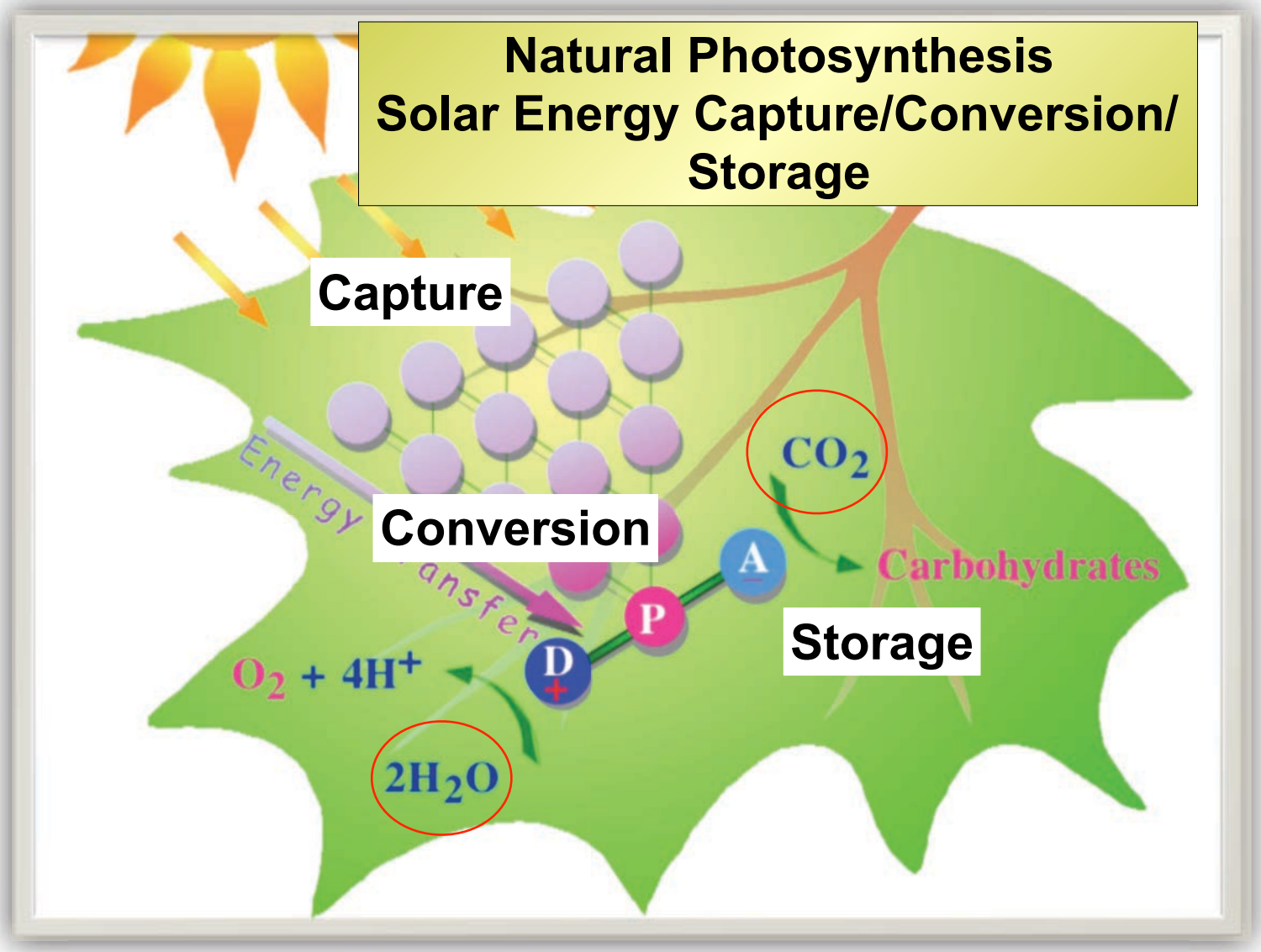
The nitrogen lone pair lies in a lower energy orbital

Chem. Eur. J. 2002, 8, 1015



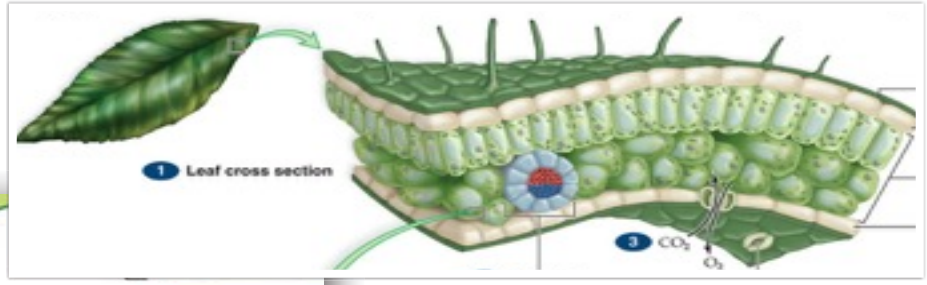
generation of charge-separated states

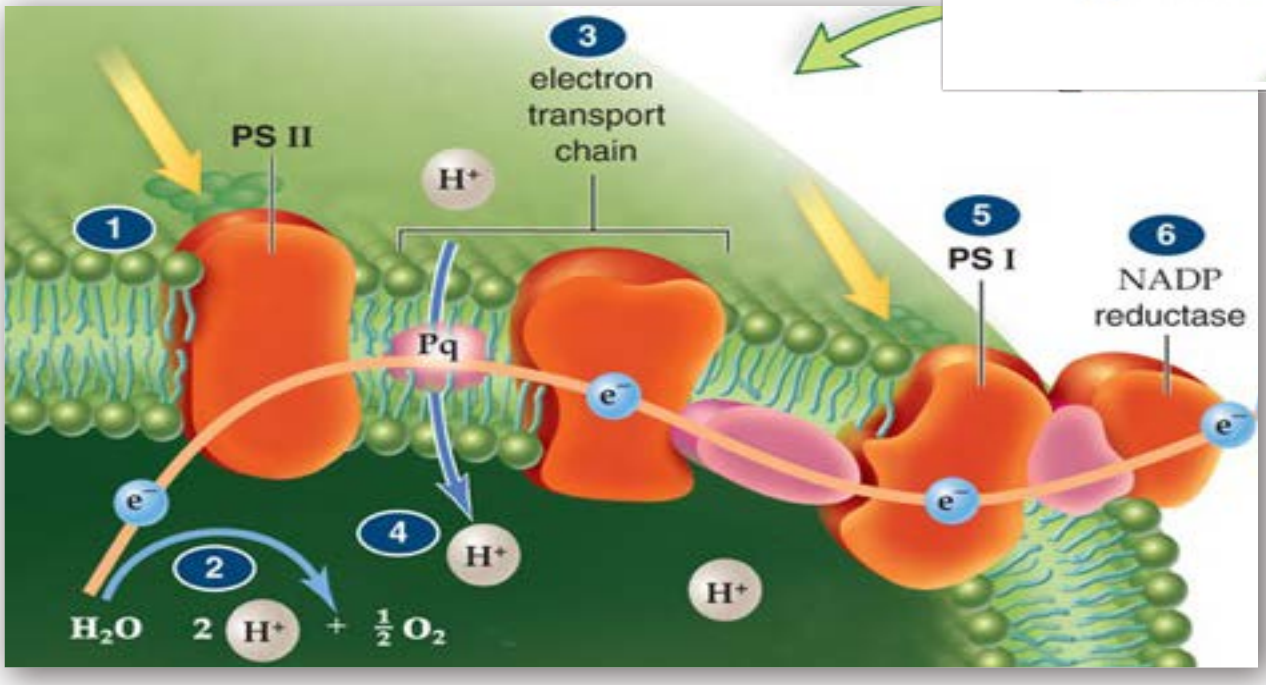
Natural Photosynthesis
Solar Energy Capture/Conversion/ Storage



Photosynthesis: a lesson from plants

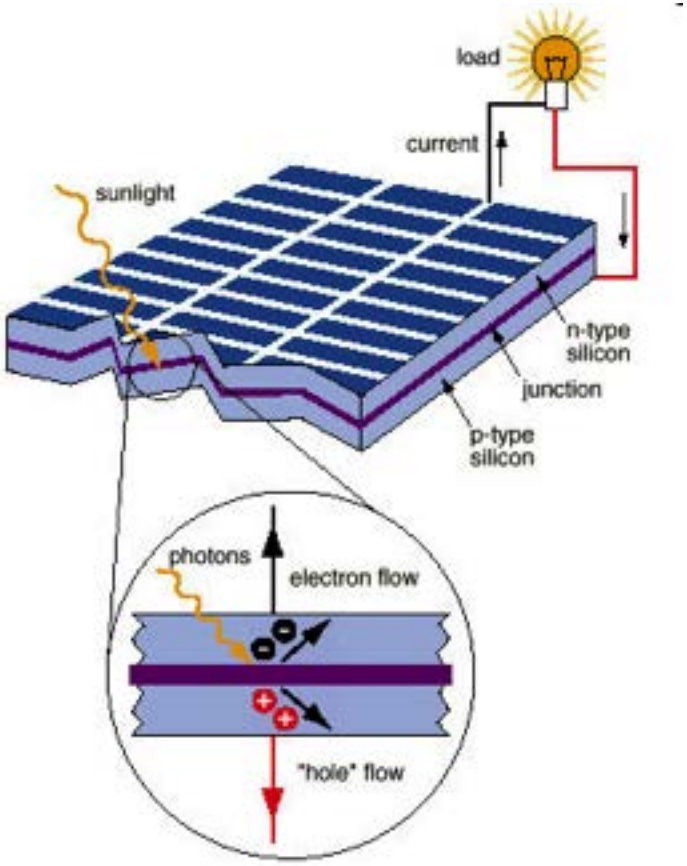
$$6\,H_2O + 6\,CO_2 + 48\,h\nu \longrightarrow C_6H_{12}O_6 + O_2$$





anatomia di una cella solare al silicio

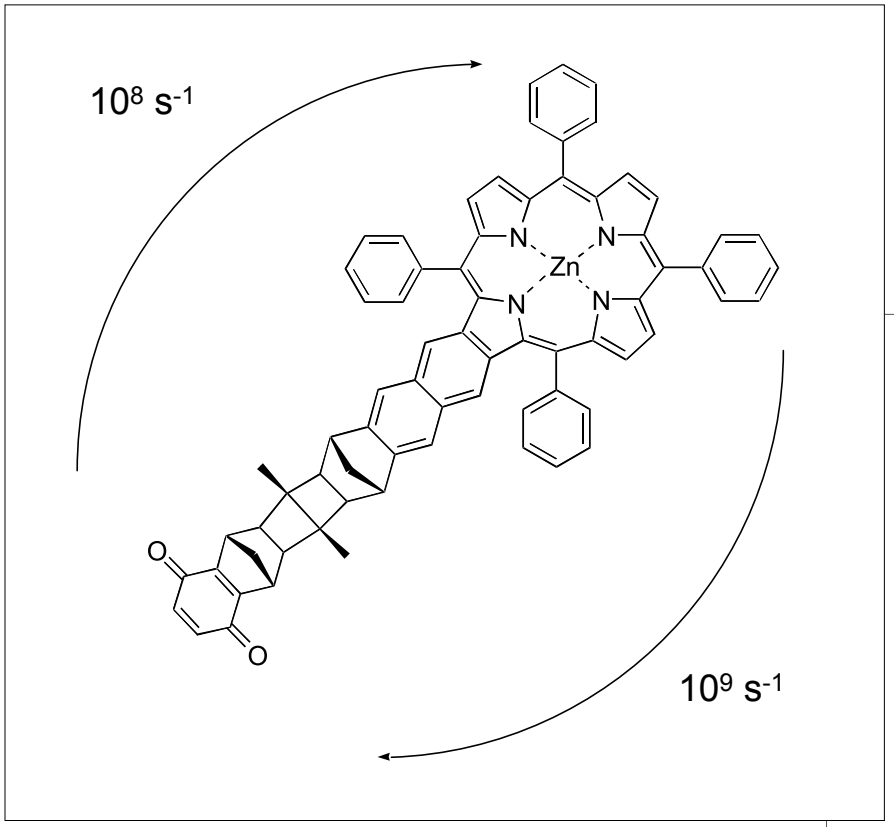
La fotocorrente è un flusso di elettroni nel silicio generato dai fotoni della luce solare



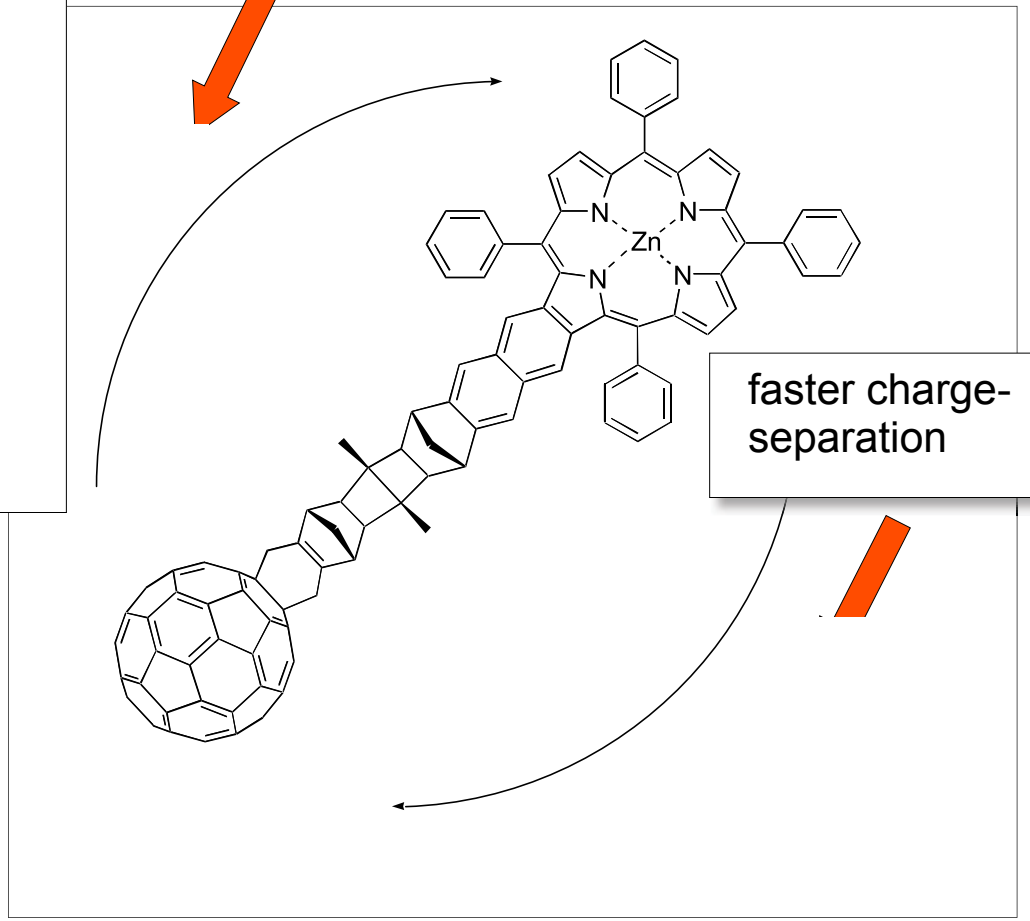
tecnologia facile, accessibile, incentivata

costo e disponibilità del silicio

ampie superfici



slower charge-recombination



faster charge-separation

Paddon-Row MN in Vögtle F. et al. *Stimulating Concepts in Chemistry*, Wiley-VCH, Weinheim, 2000

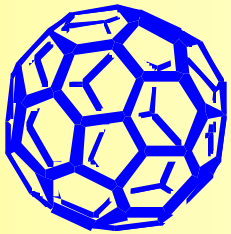
C_{60} is an ideal partner in photoinduced processes because:

a) is a good electron acceptor

b) has readily accessible excited states (singlet and triplet)

c) becomes a much better acceptor in the excited states

d) has a low reorganization energy



as is

heterogeneous mixtures
(conducting polymers,
phthalocyanines, etc)

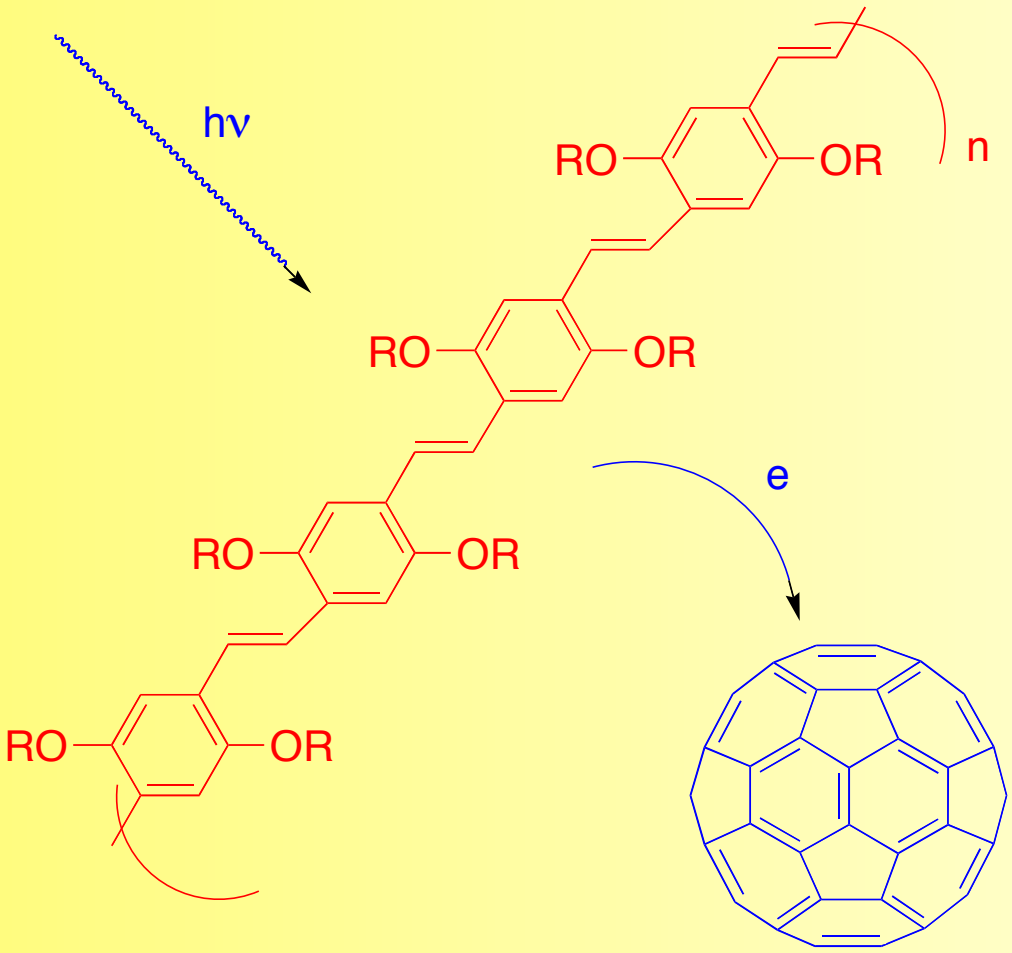
solar cells
photoconductors
photosynthesis

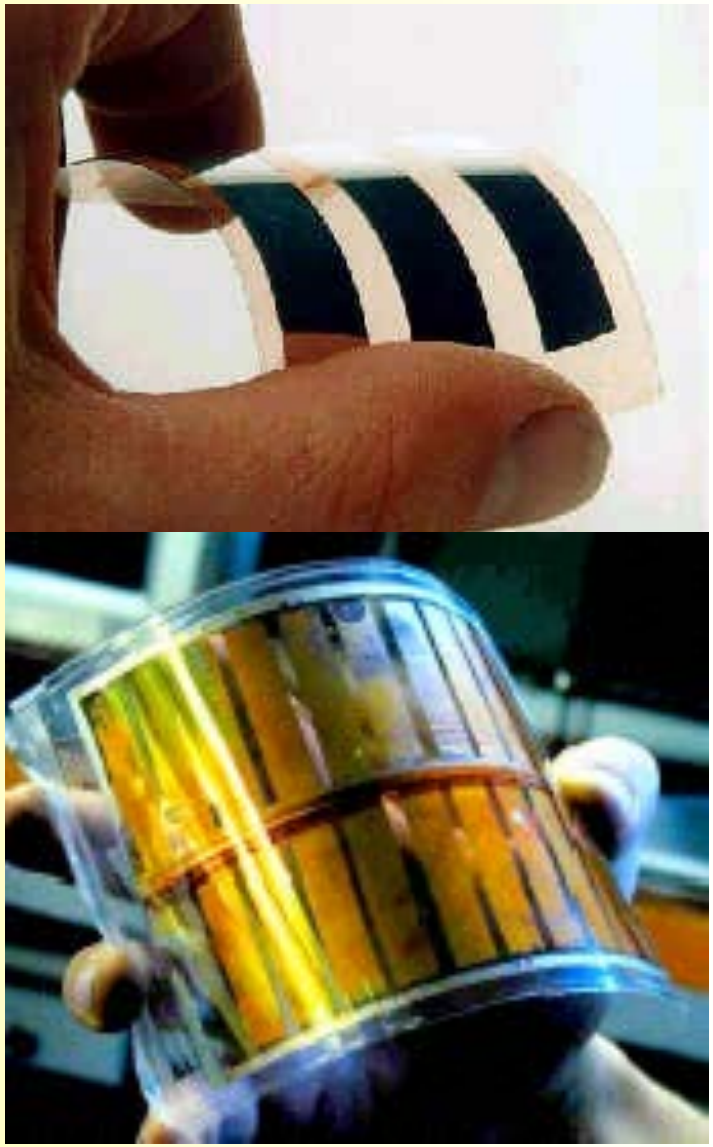
chemical derivatization

heterogeneous mixtures
(conducting polymers, etc)
dyads, triads
(donors and C_{60} covalently attached)

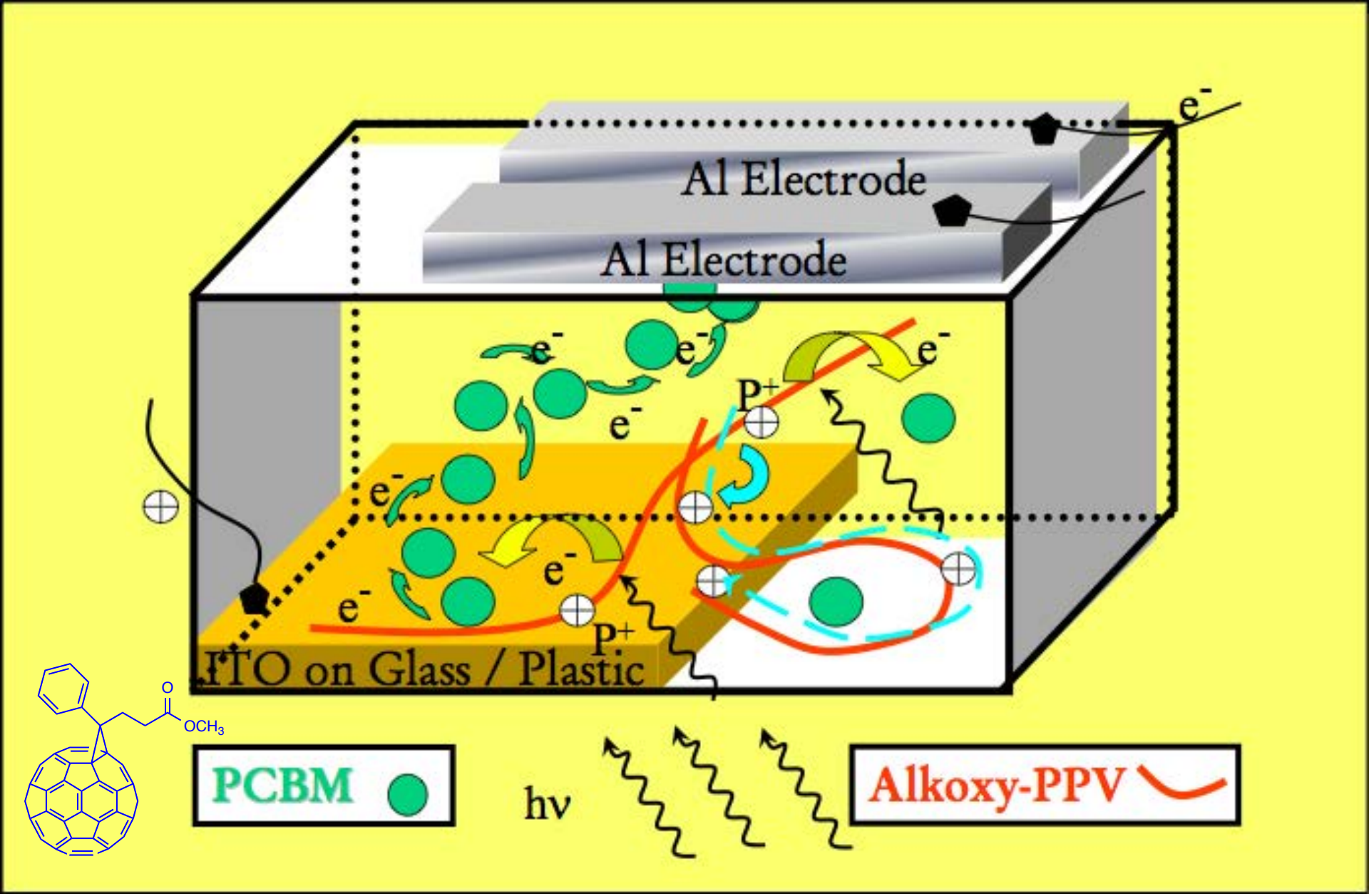
solar cells
photoconductors
photosynthesis

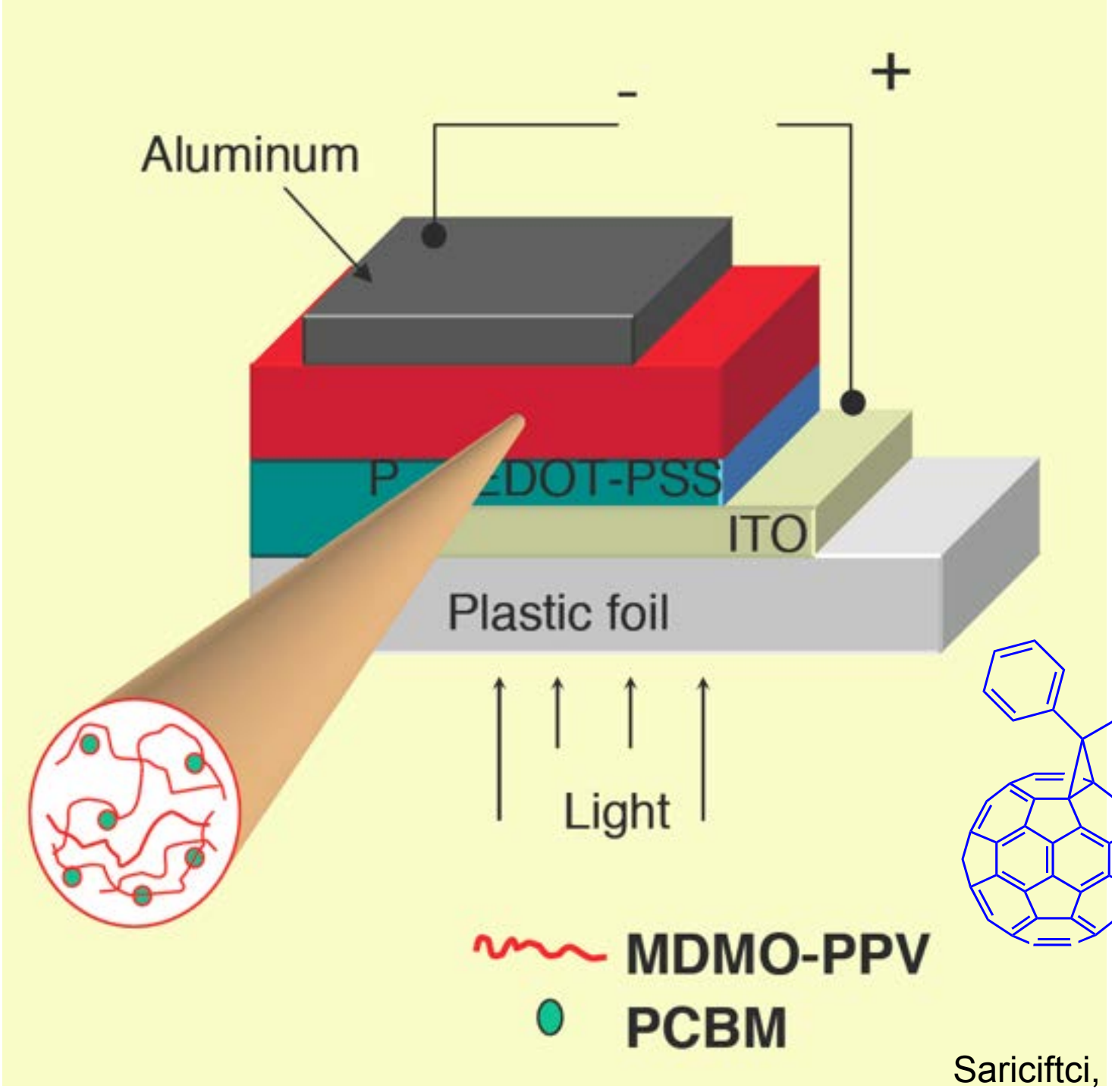
Molecular Plastic Solar Cells



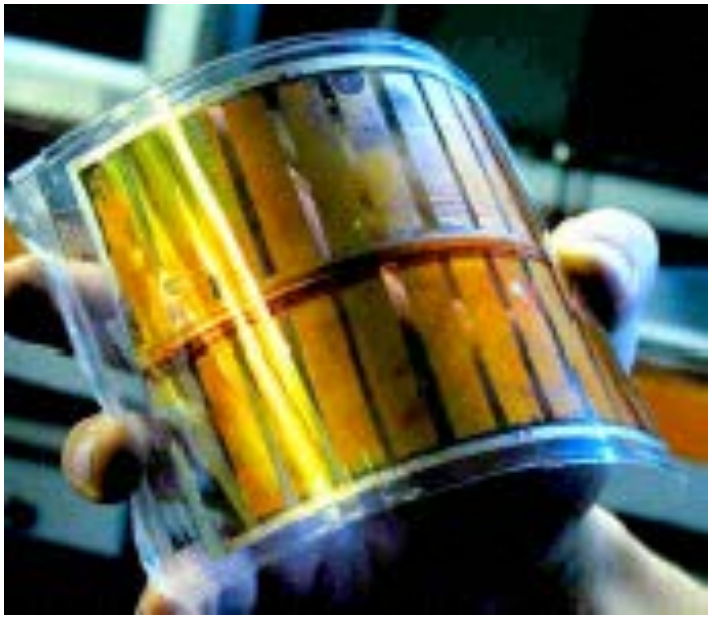


Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. Science **1992**, 258, 1474-1476

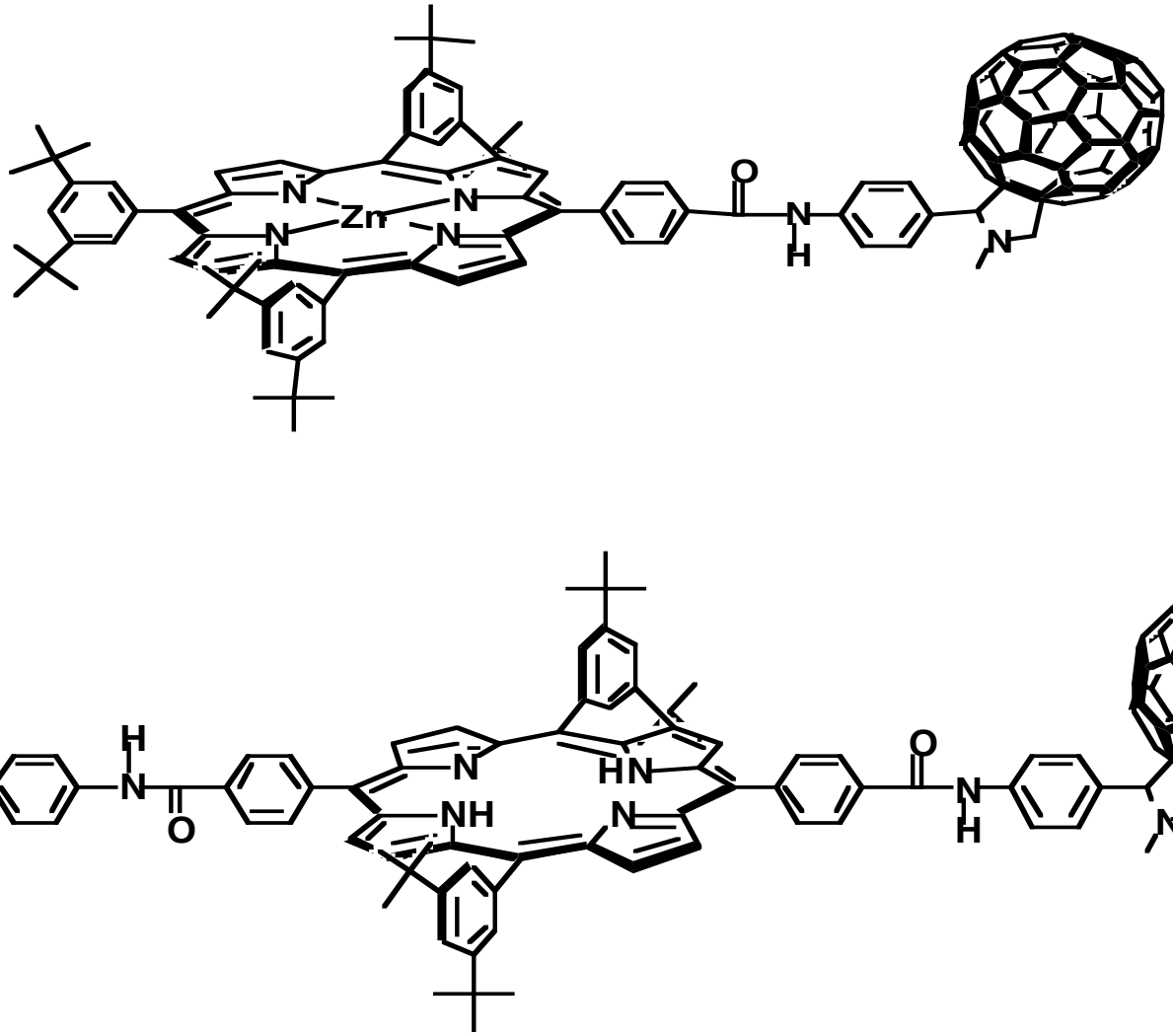

e-
Al Electrode
Al Electrode
e-
e-
e-
e-
e-
e-
e-
e-
P+
P+
ITO on Glass / Plastic
O
OCH3
PCBM
hν
Alkoxy-PPV



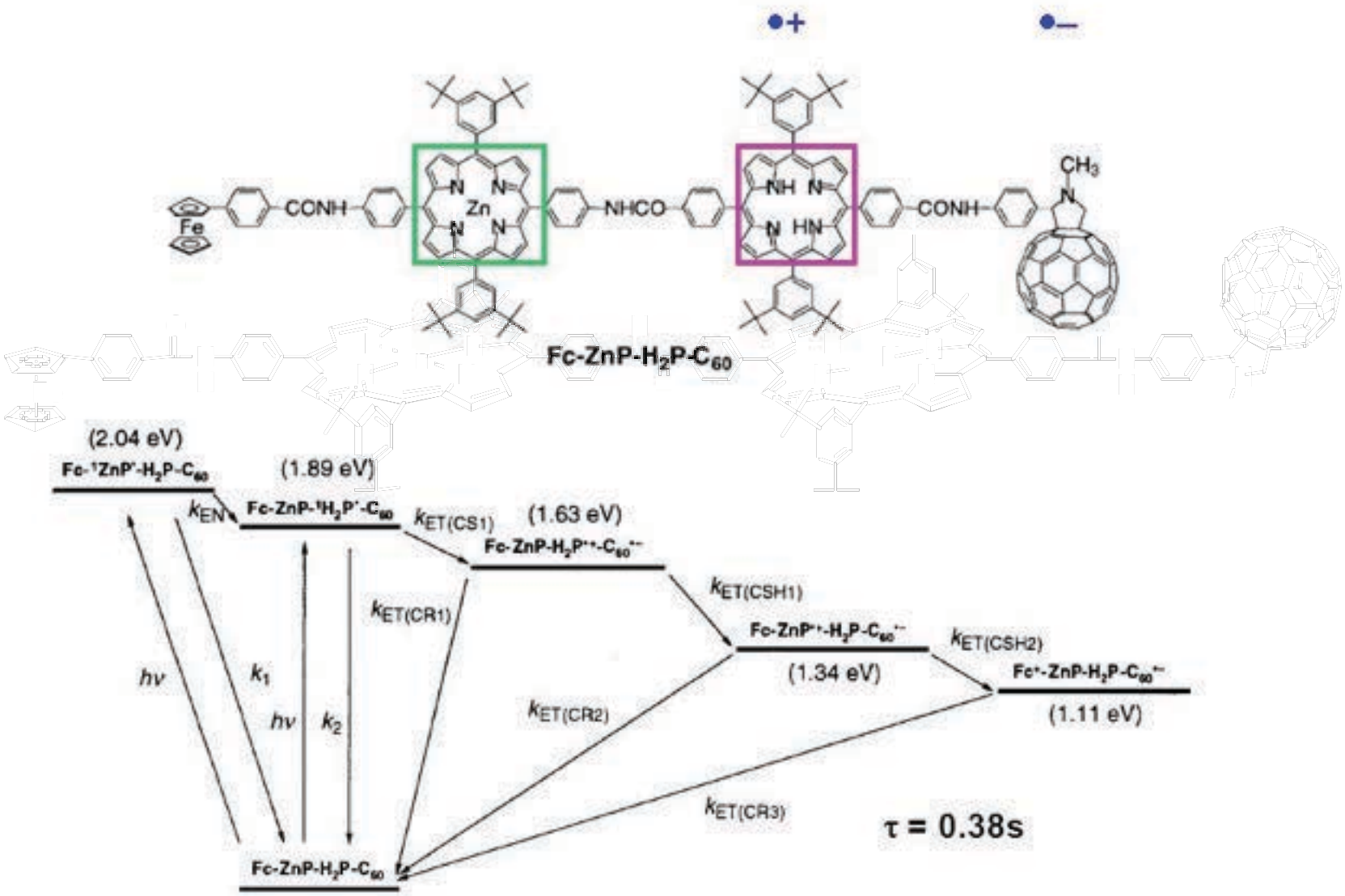
Sariciftci, N. S., et al.



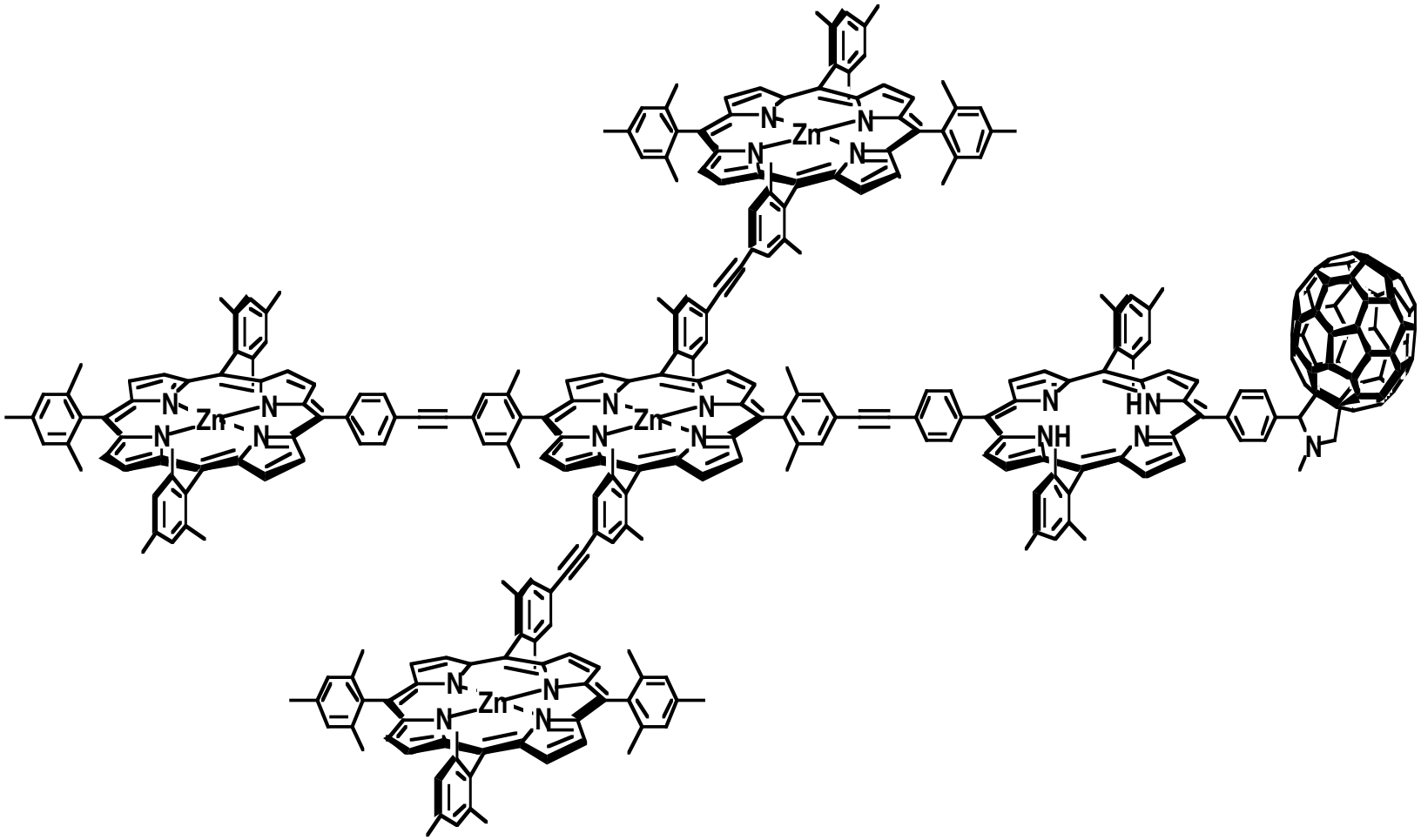
4% Yield
Prof. N S Sariciftci
Linz University, Austria


N
Zn
N
N
N
O
N
H
N
H
N
O
Fe
N
HN
NH
N
O
N
H
N

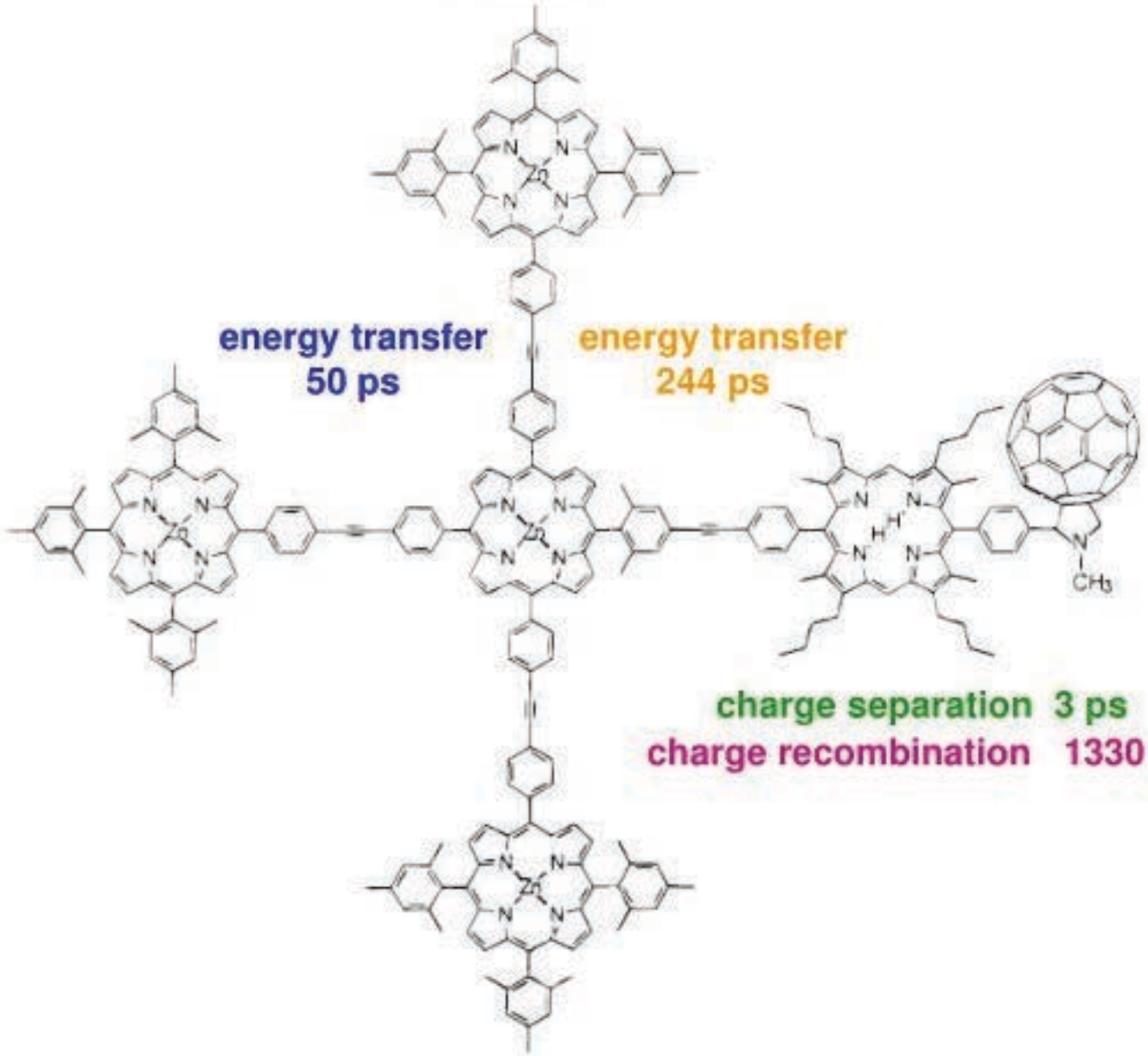
Tetrad



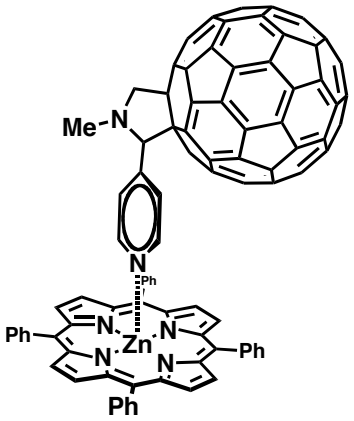
Fukuzumi.S, Guldi,D.M et al, J.Am.Chem.Soc. **2001**, *123*, 6617


N
Zn
N
N
N
HN
NH
N

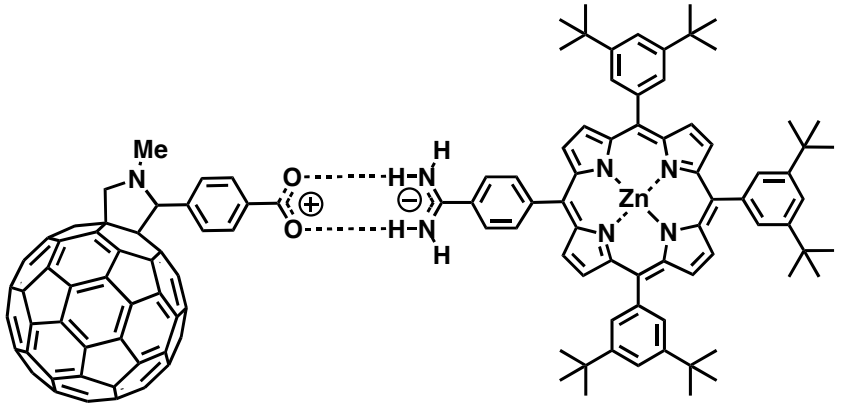
Hexad



Gust. D., Lindsey.J, et al, J.Am.Chem.Soc. **1999**, *121*, 8604



9



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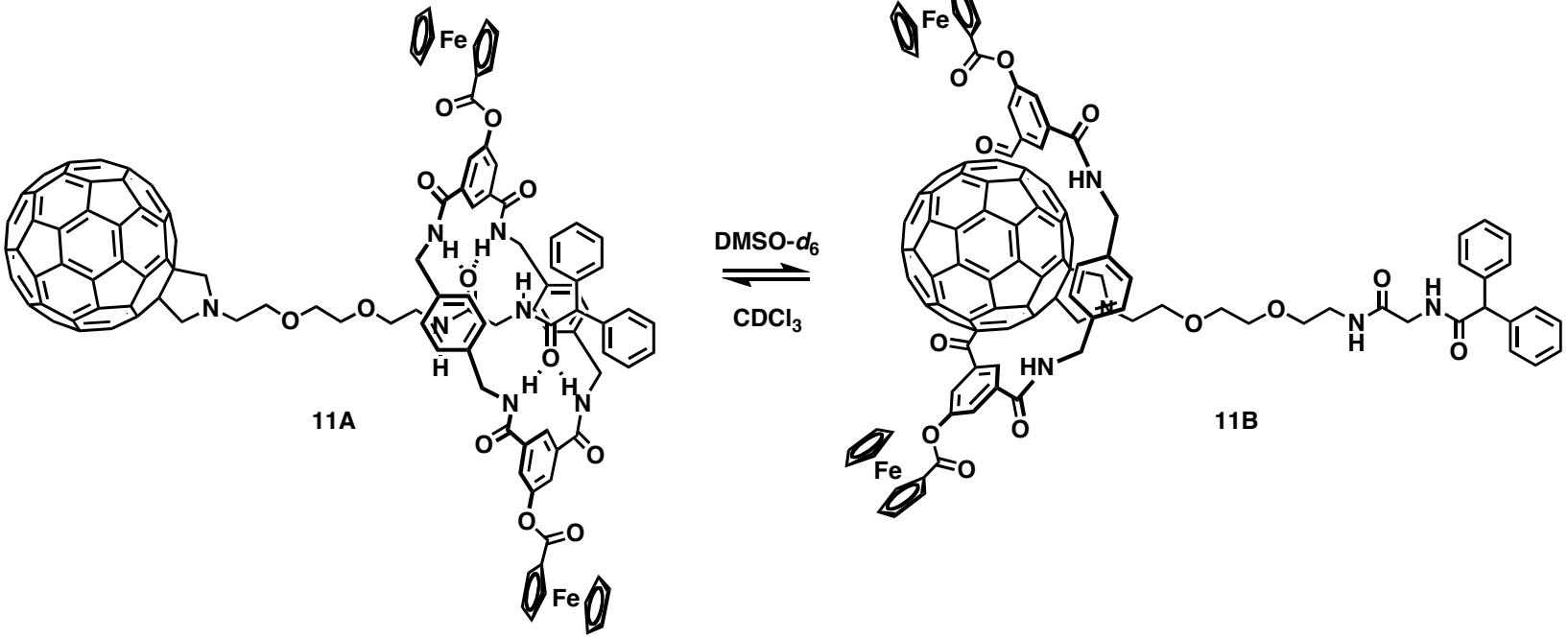
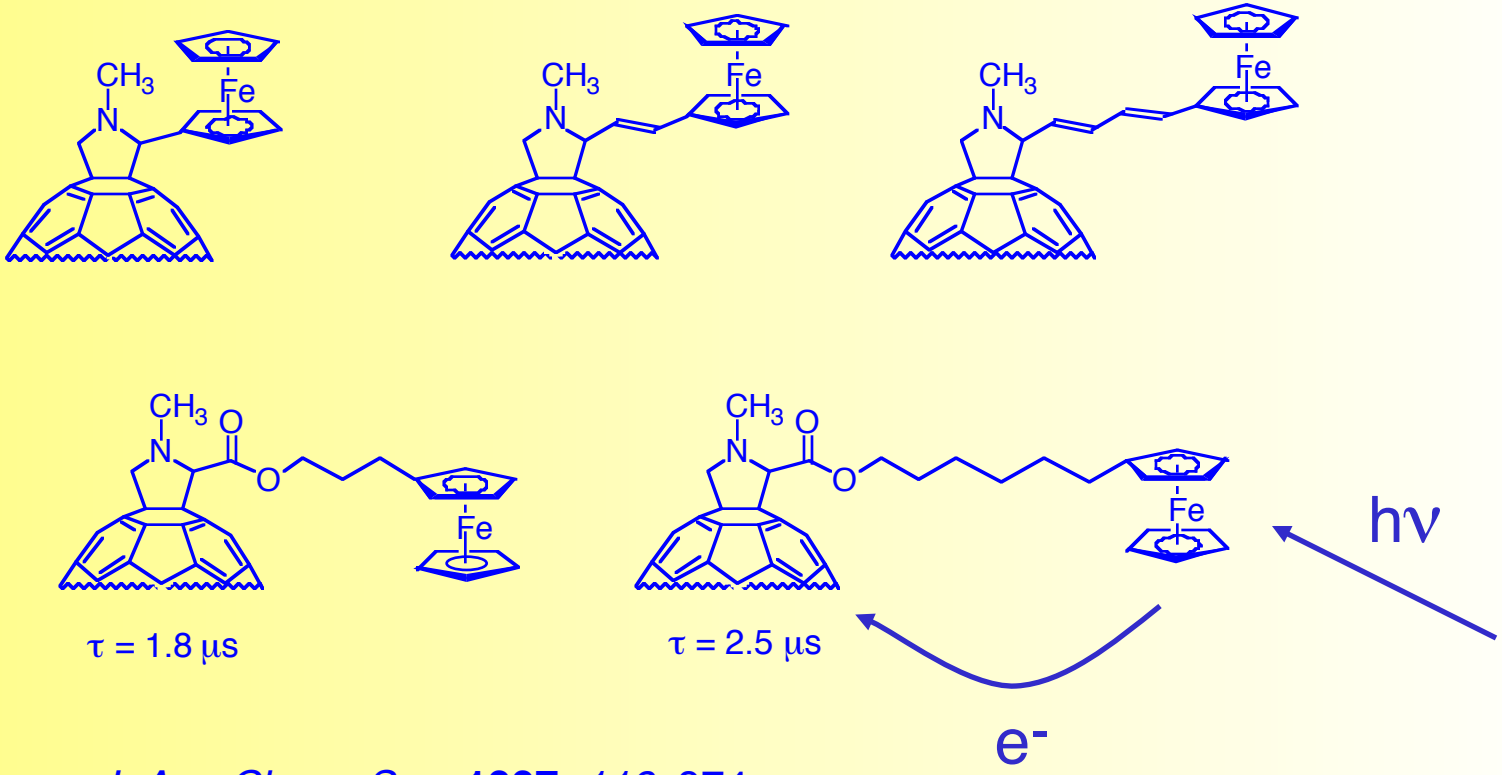


11A

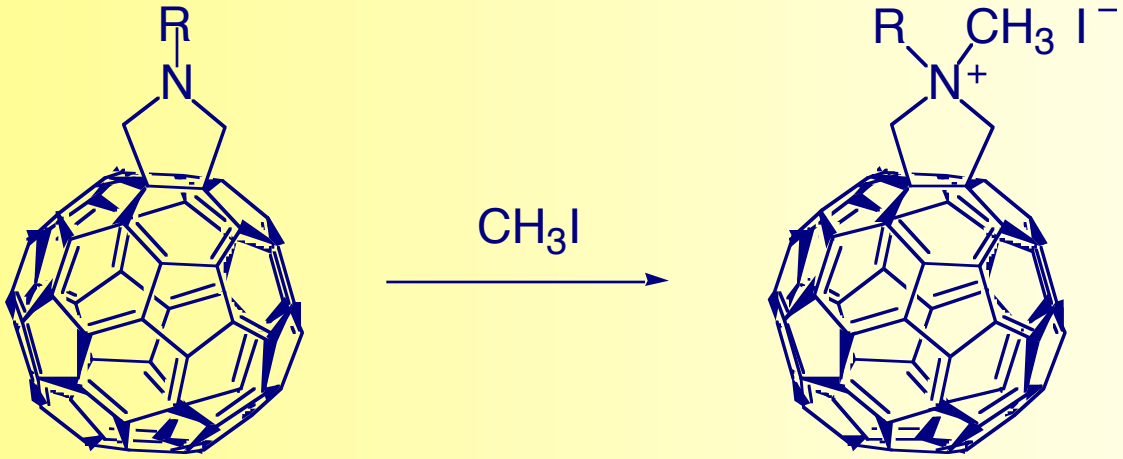
11B

Light-Induced Electron-Transfer and Charge-Separation in Fullerene-Ferrocene Dyads



J. Am. Chem. Soc. **1997,** *119*, 974

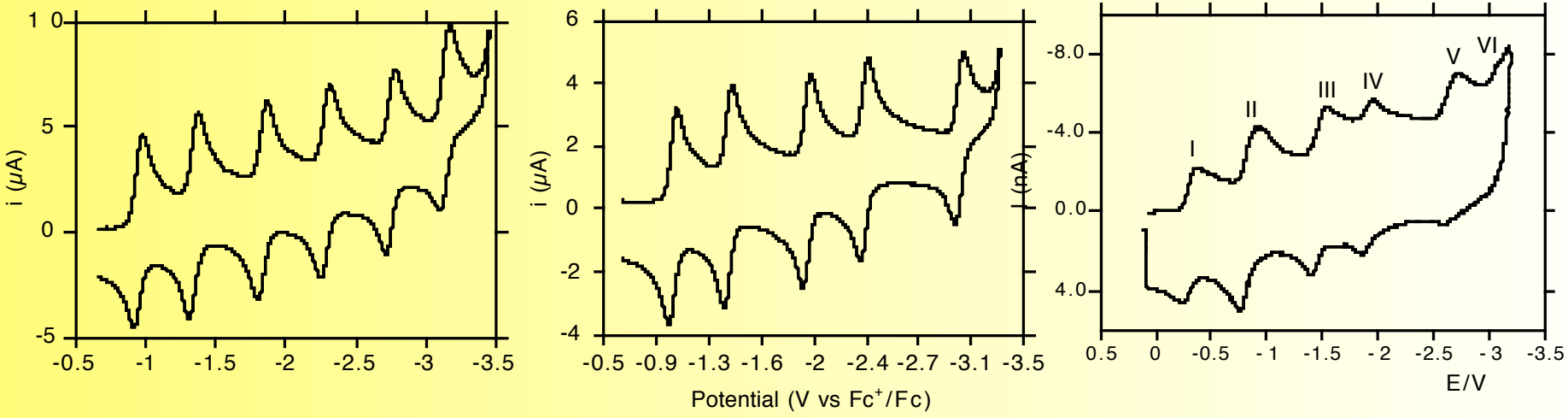
N-Me-Fulleropyrrolidinium Ions are Better Acceptors



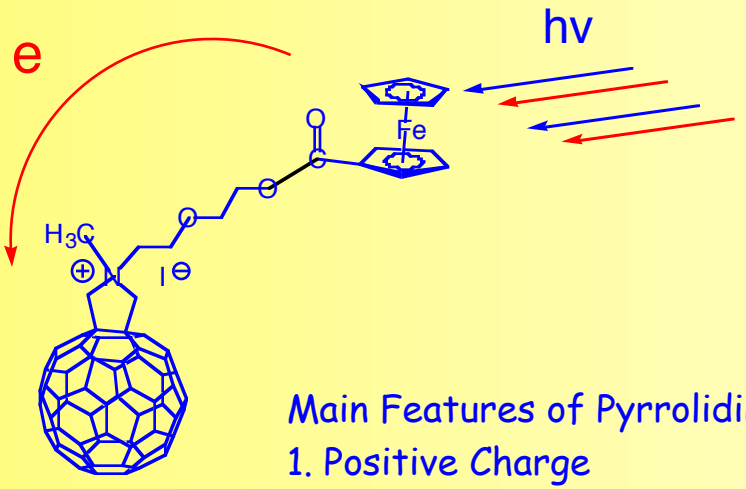
E1/2 values (V vs SCE) -0.47 -0.29

C_{60} -0.35

J. Am. Chem. Soc., 1998, 120, 11645



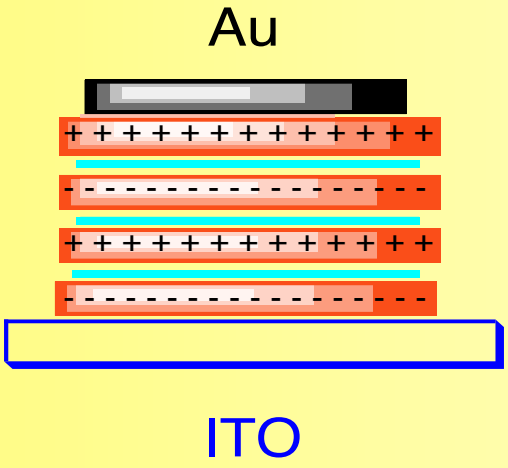
Advantages of using fulleropyrrolidinium ions in photo-optical devices

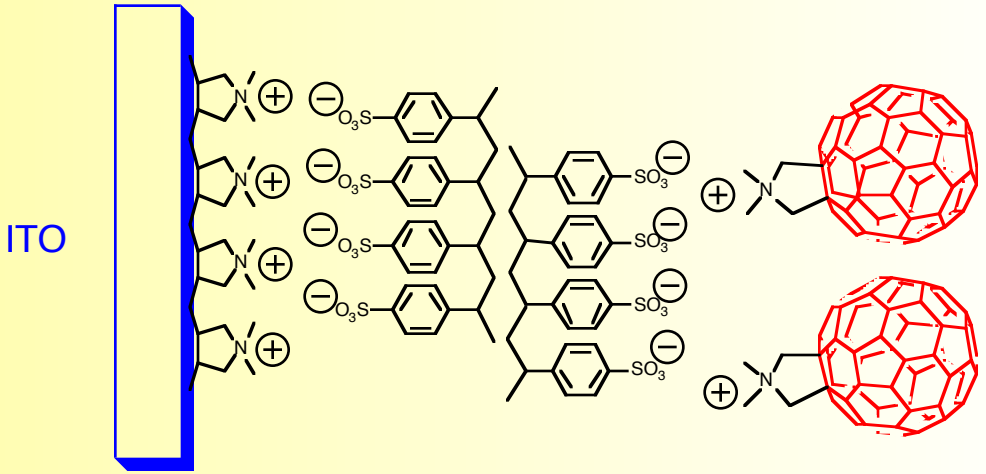


Main Features of Pyrrolidinium Ions
1. Positive Charge
2. Strong Acceptor Character

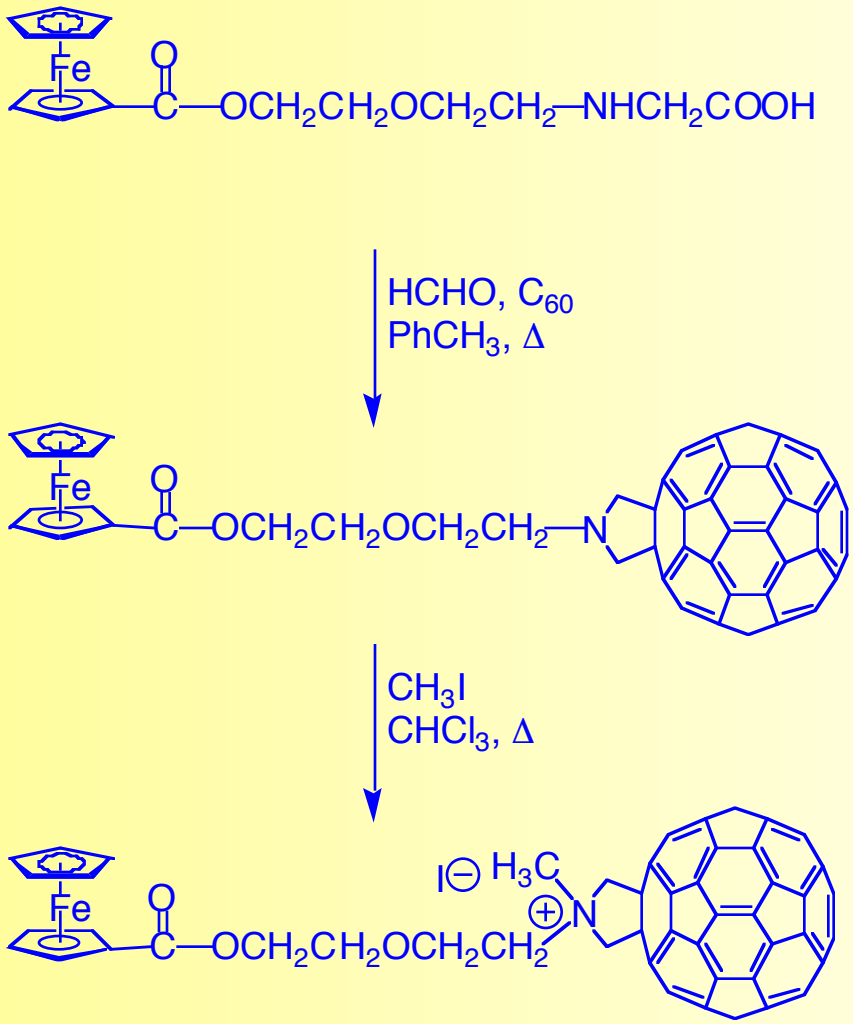
⟹

Suitable for Self-Assembly of Ordered Multilayers Driven by Electrostatic Forces

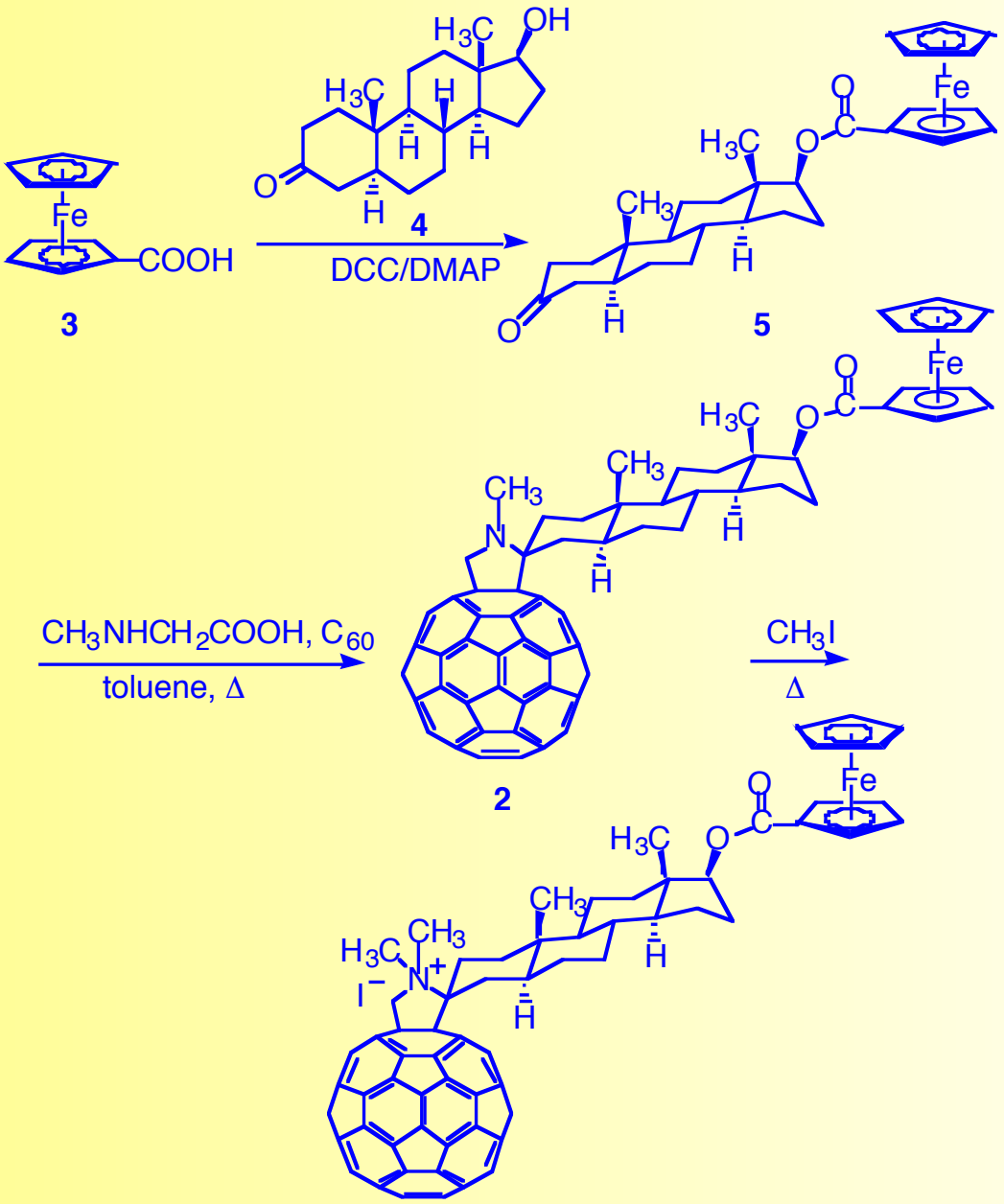




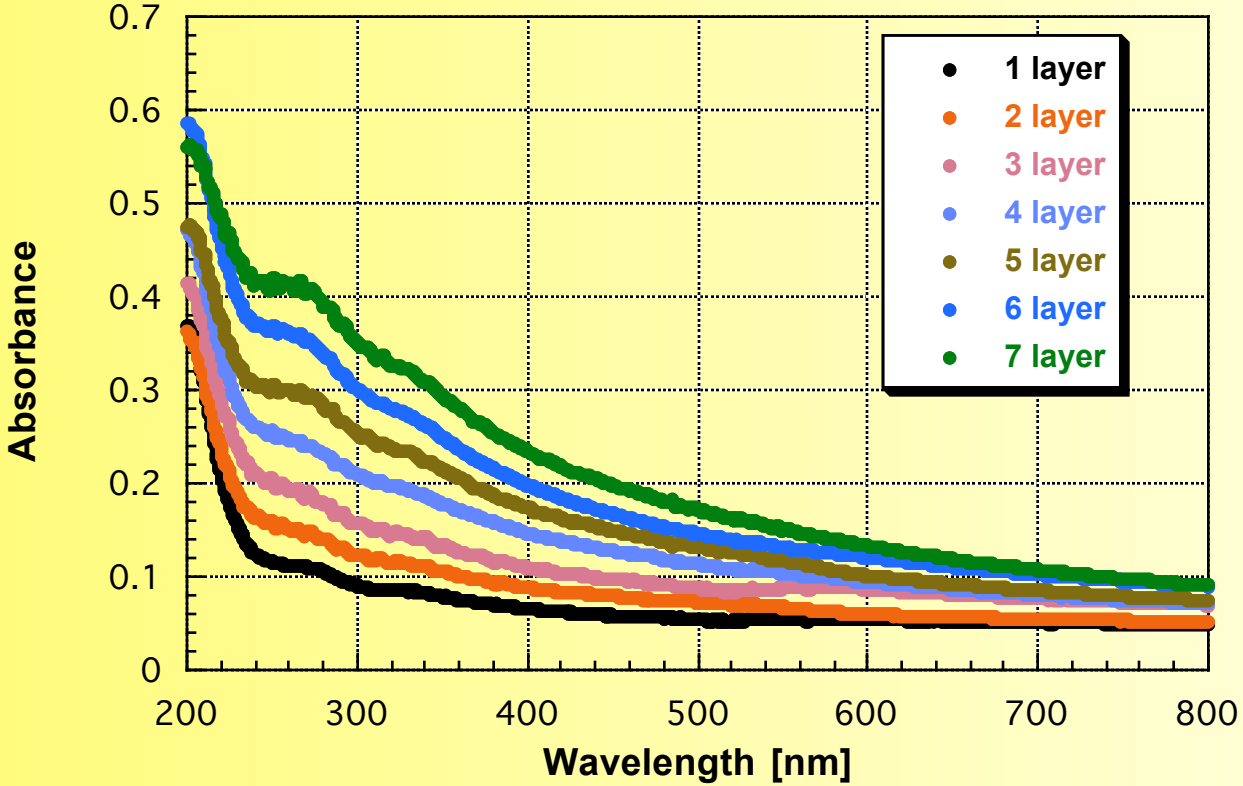
Synthesis of a Ferrocene-Fullerene Flexible Dyad

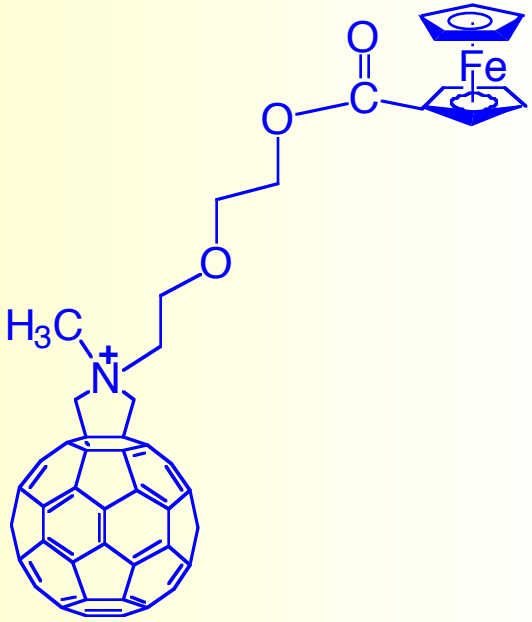


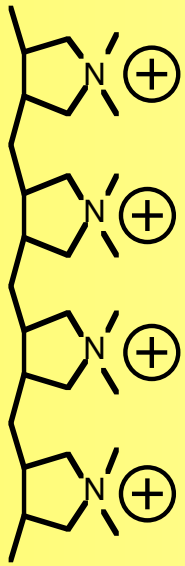
Synthesis of a Ferrocene-Fullerene Rigid Dyad

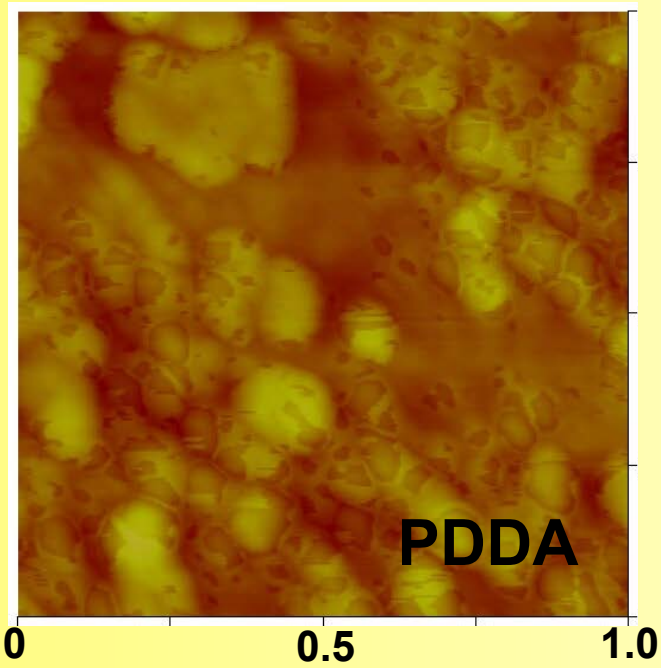


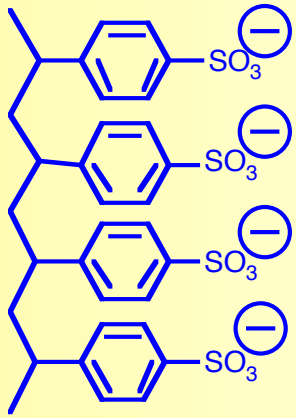
Layer-by-layer deposition of fulleropyrrolidinium ion
Evidence from Absorption Spectroscopy

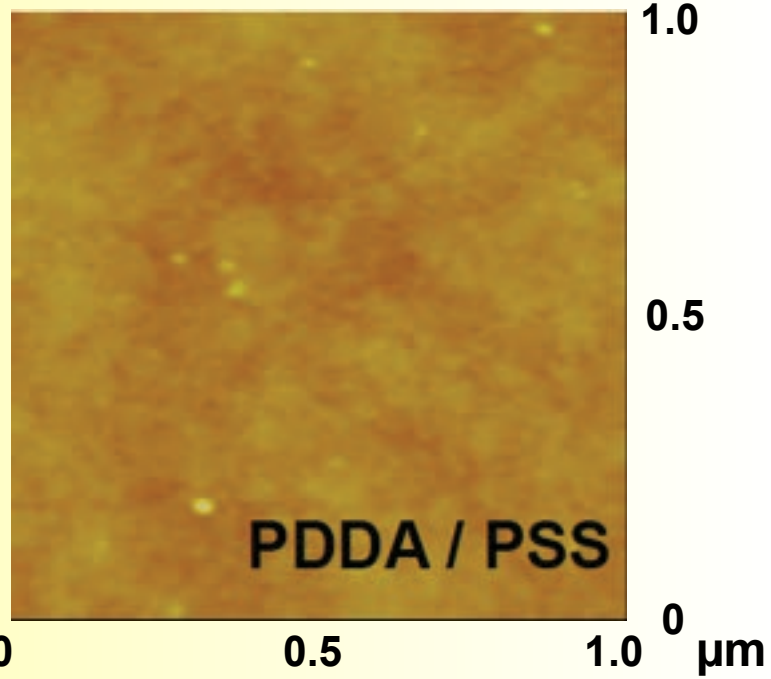








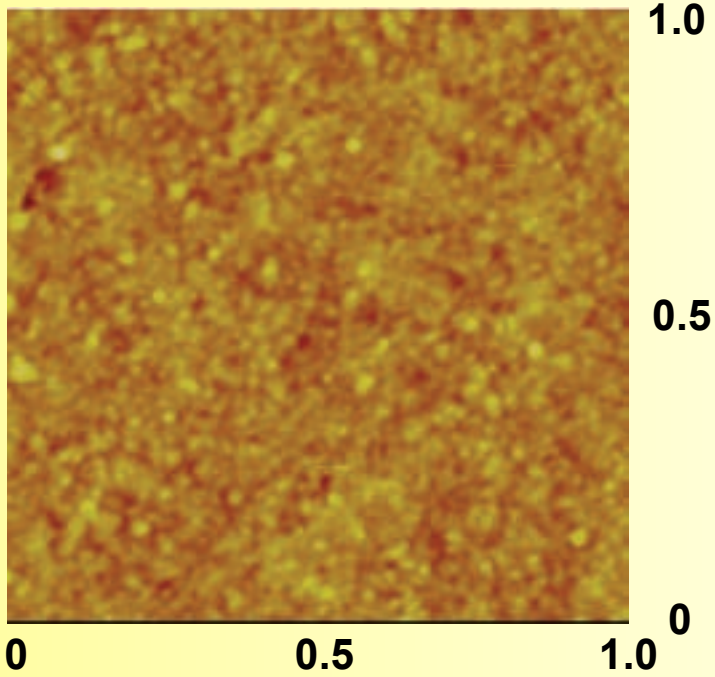


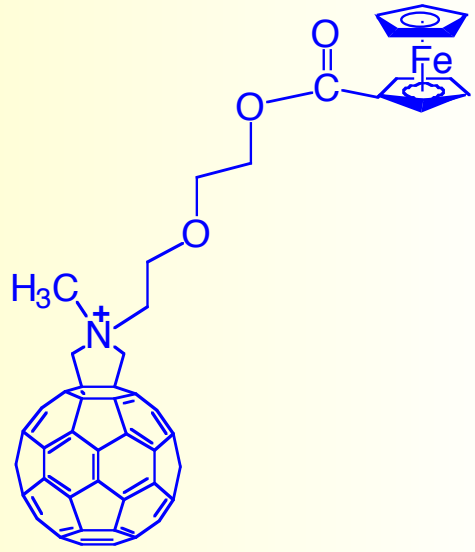


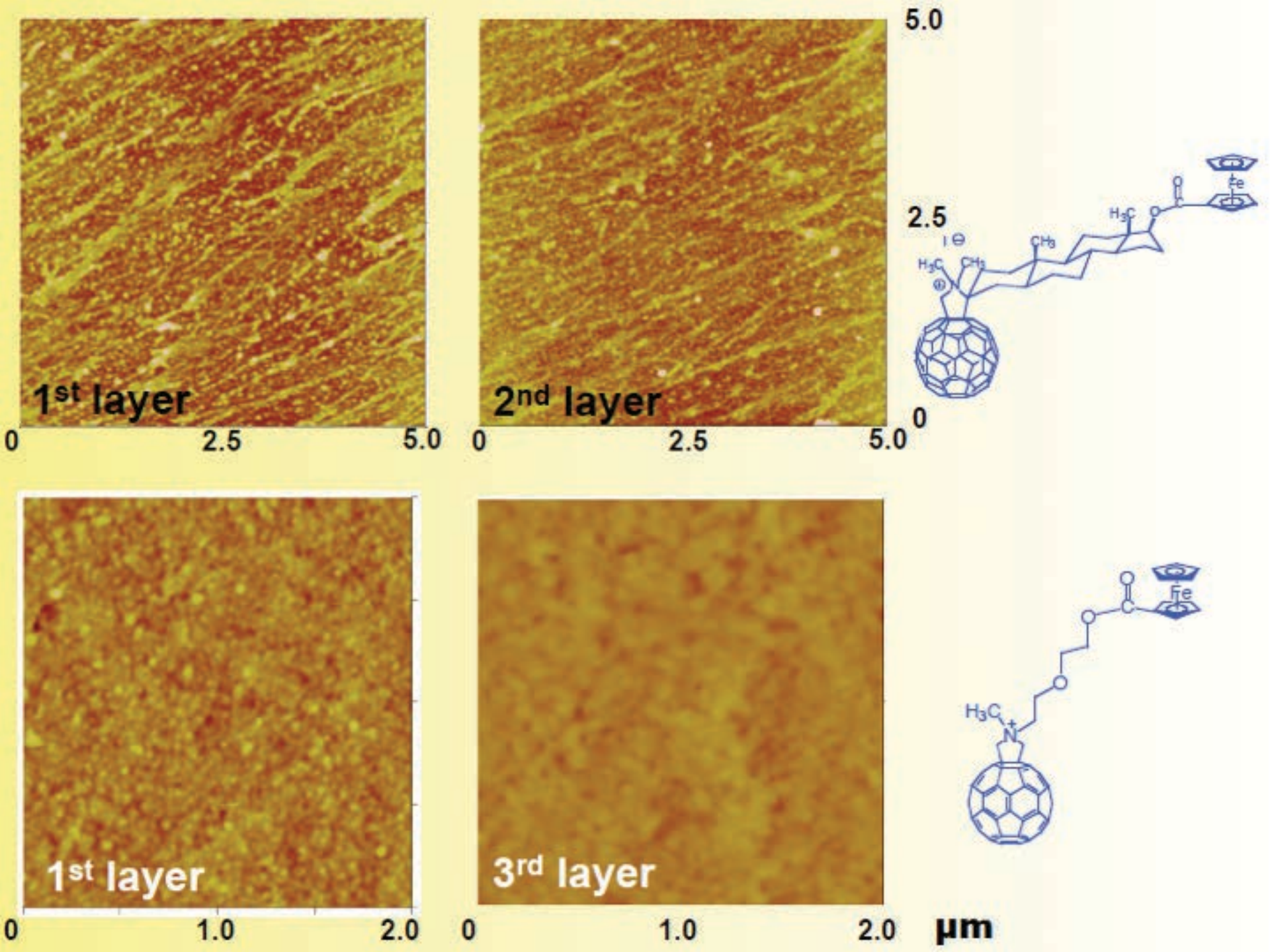
PDDA

PDDA & PSS

monolayer coverage



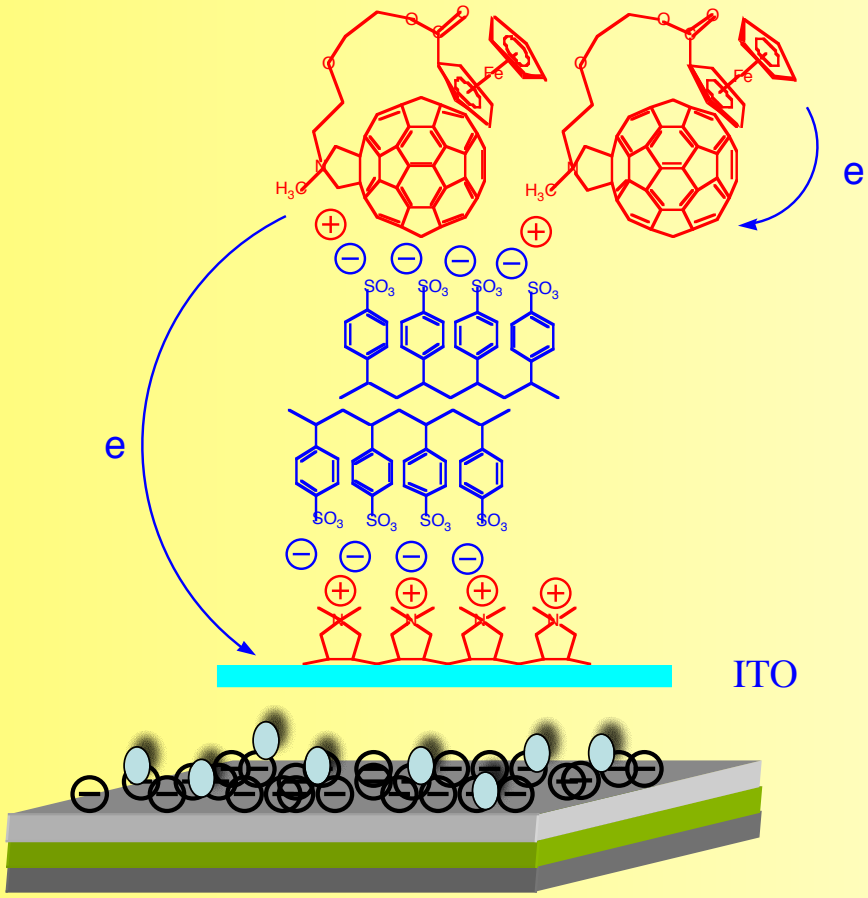


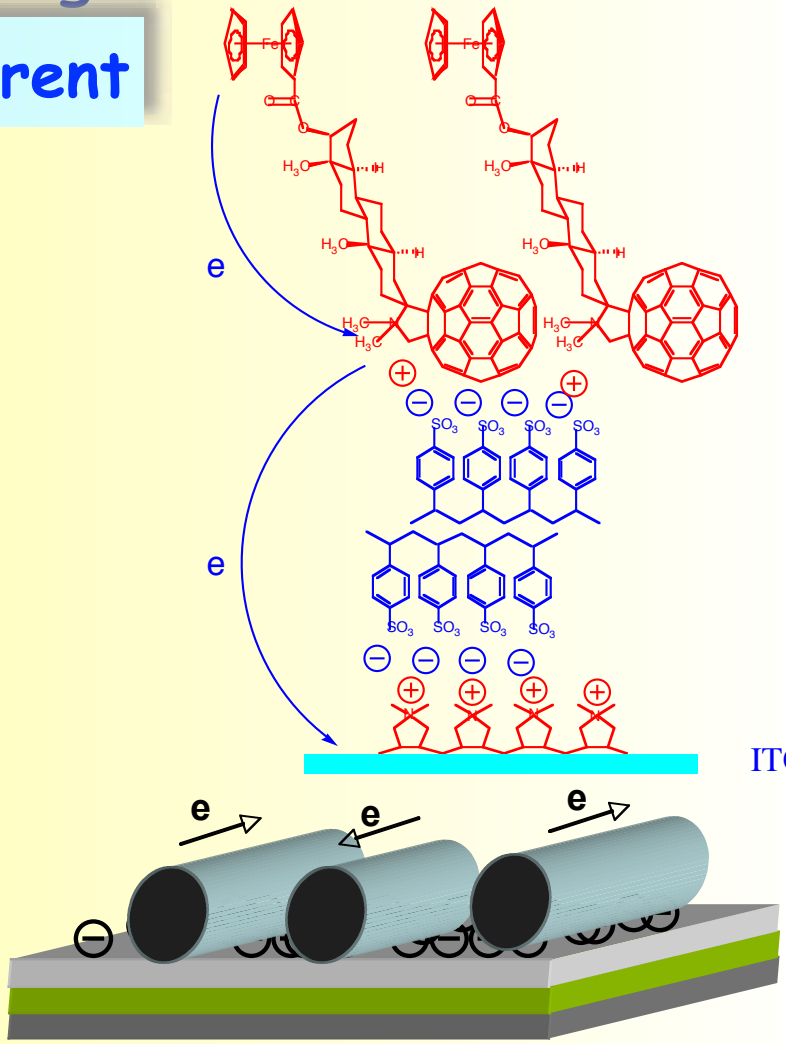

1st layer
2nd layer
1st layer
3rd layer
0
2.5
5.0
1.0
2.0
μm
Fe
I⊖

Pyrrolidinium dyads - comparison

rigid versus flexible

flexible dyad shows "0" photocurrent



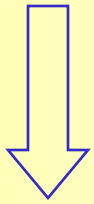


fast charge-recombination
poor charge mobility

slow charge recombination
good charge-transport

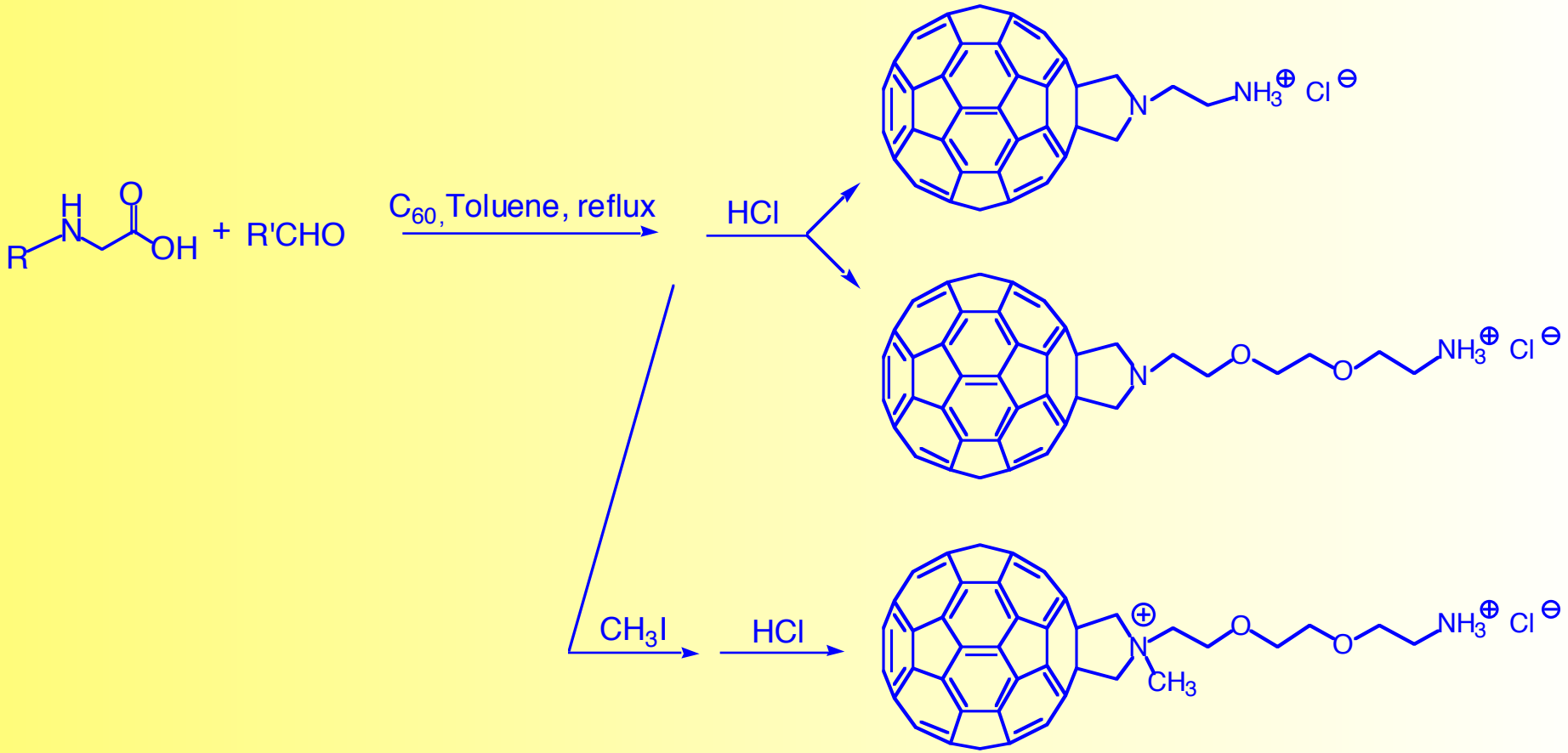
CONCLUSION

The role of the morphology in these systems is of fundamental importance



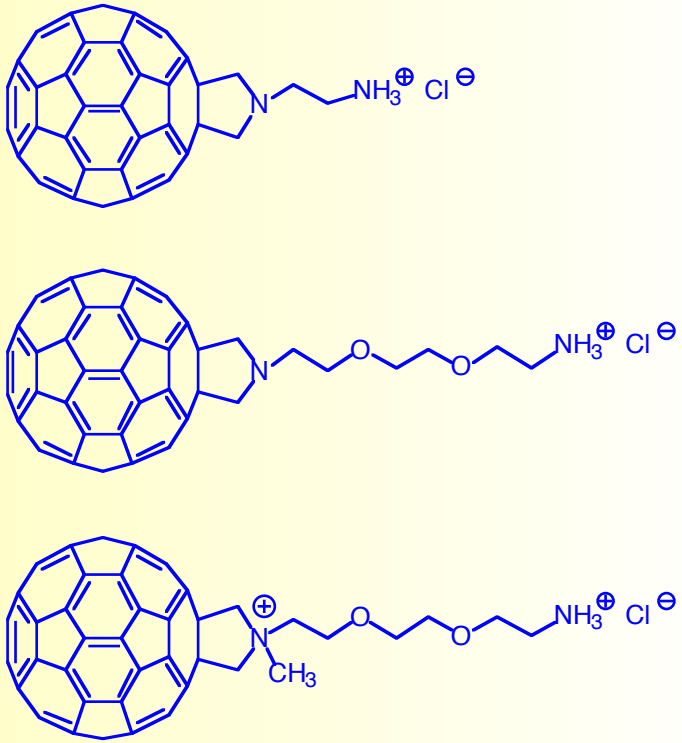
Study of the general behavior of aggregation in fullerene derivatives

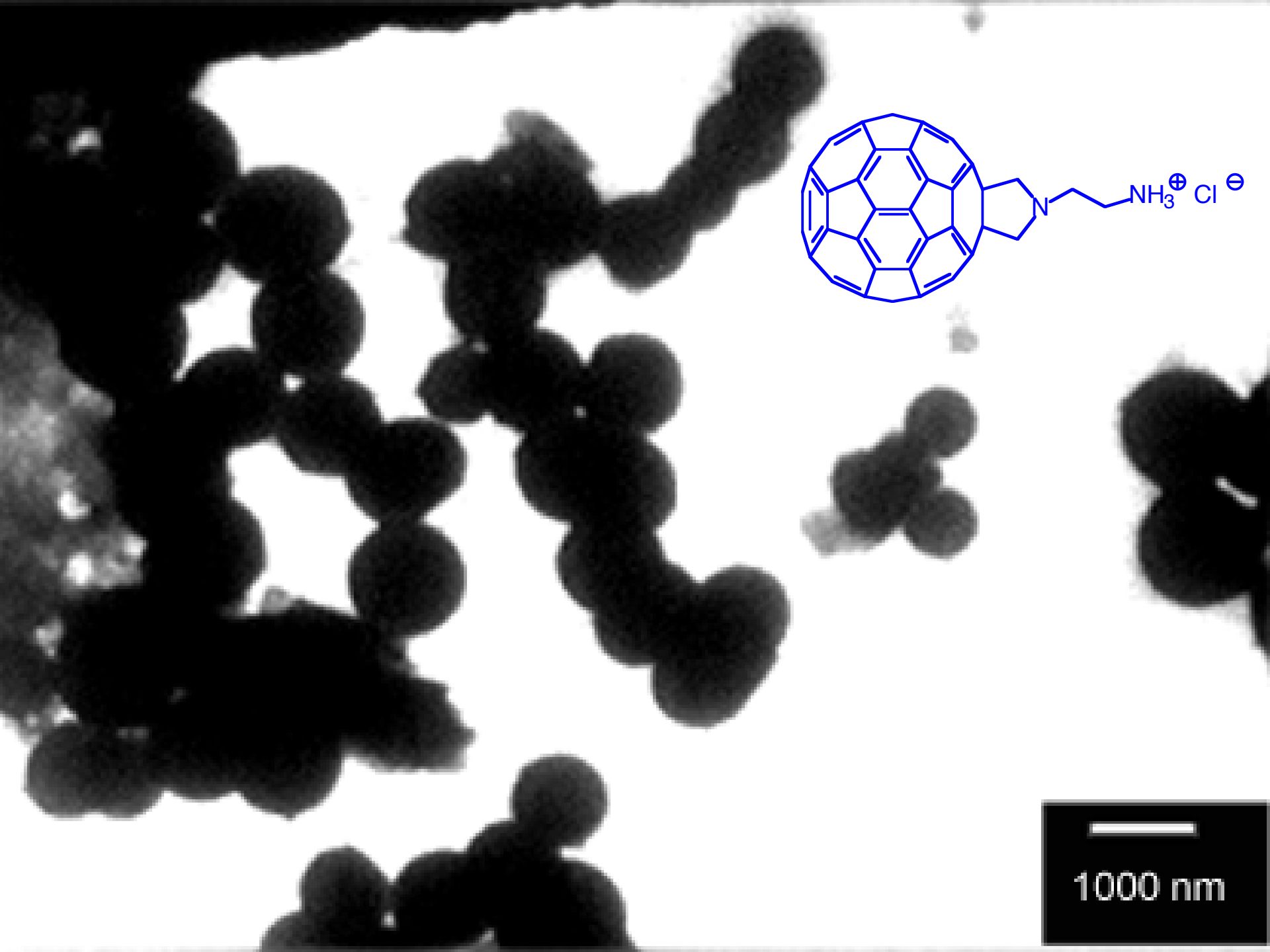
Synthesis of Novel Amphiphilic Fullerene derivatives

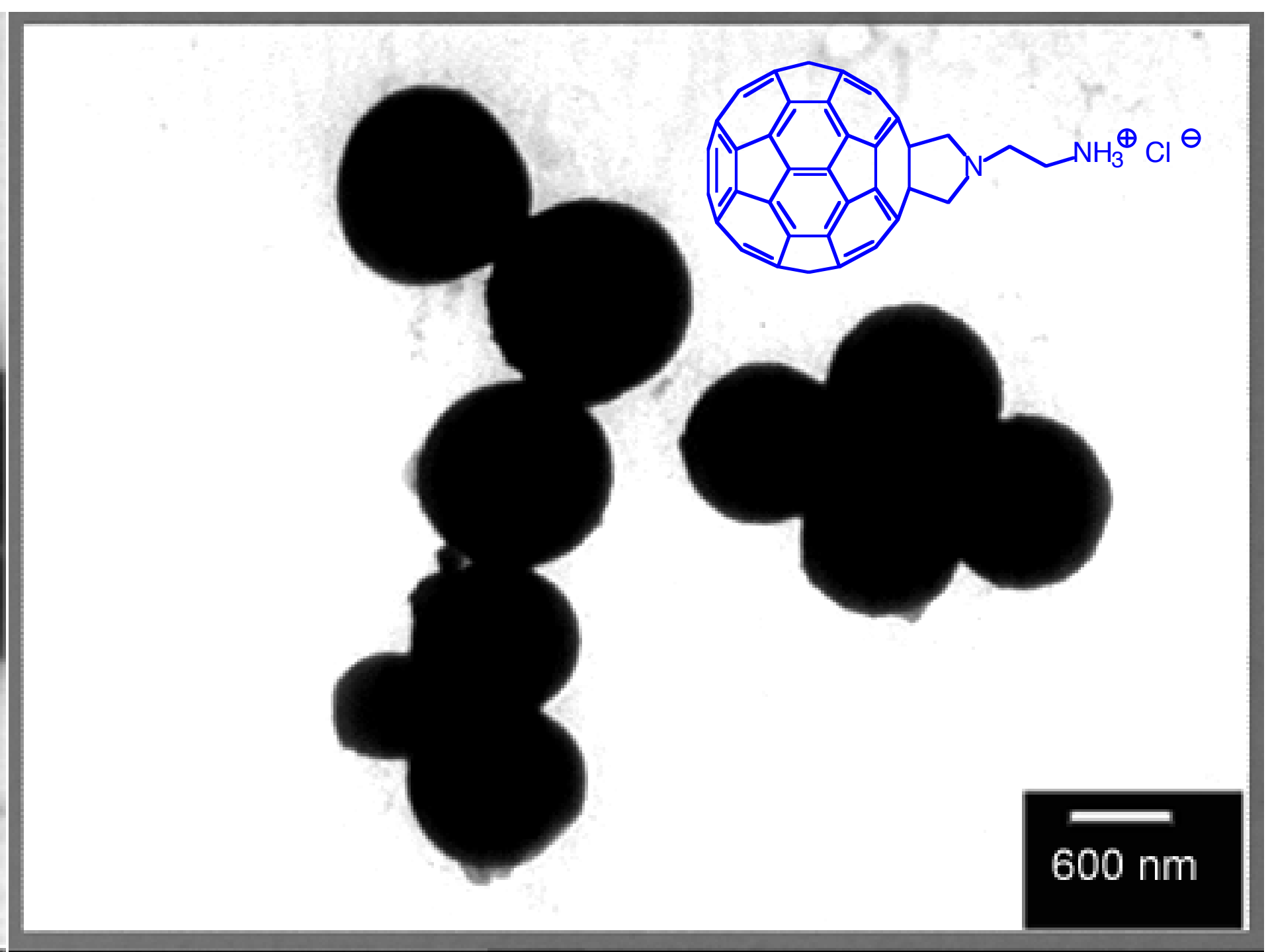


Preparation of the samples

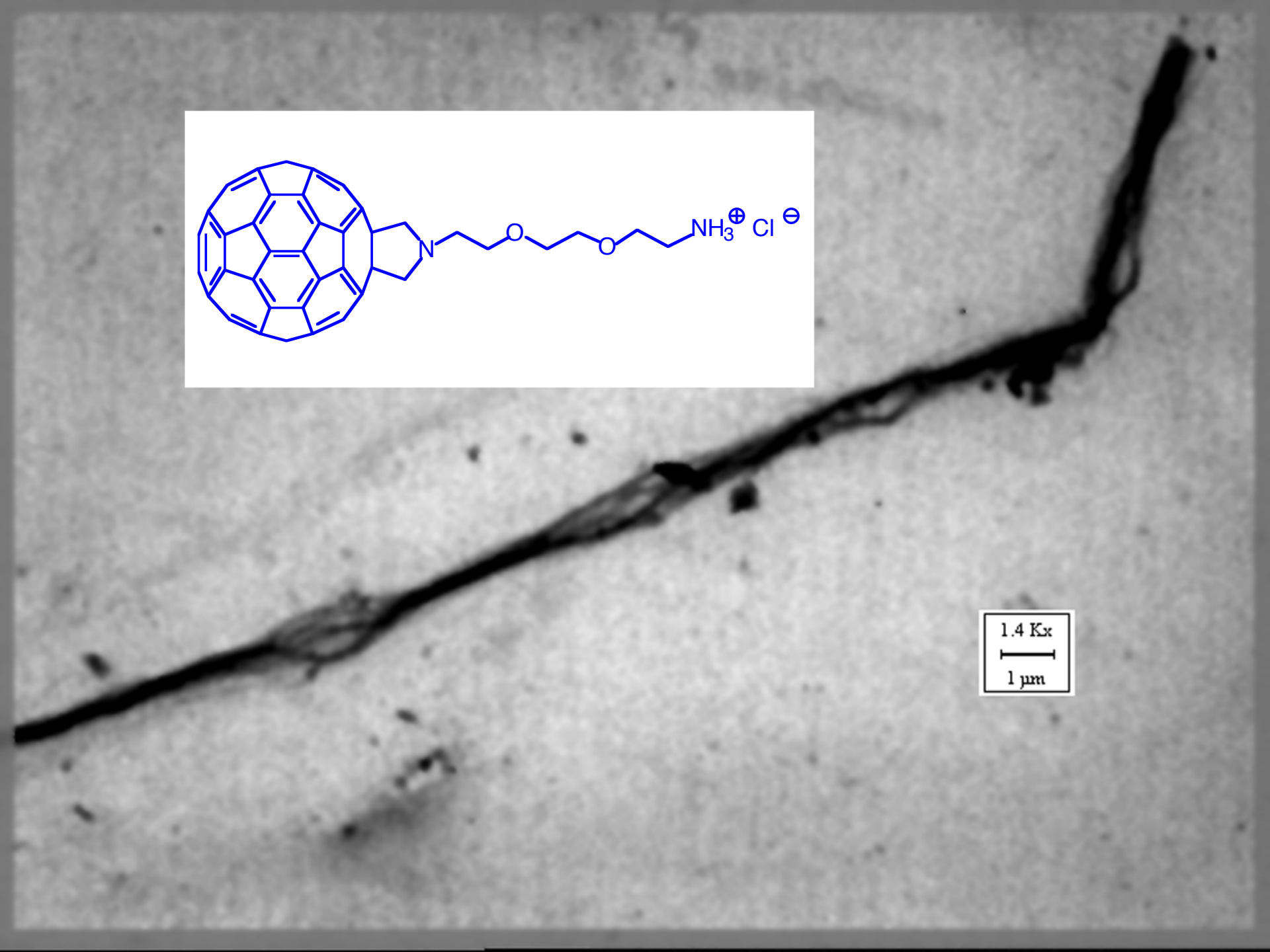
1. Suspended in water
2. Sonicated in a water bath
3. Centrifuged @ 3,000 rpm
4. A drop deposited on a TEM grid
5. Wait for solvent evaporation
6. Look and wonder

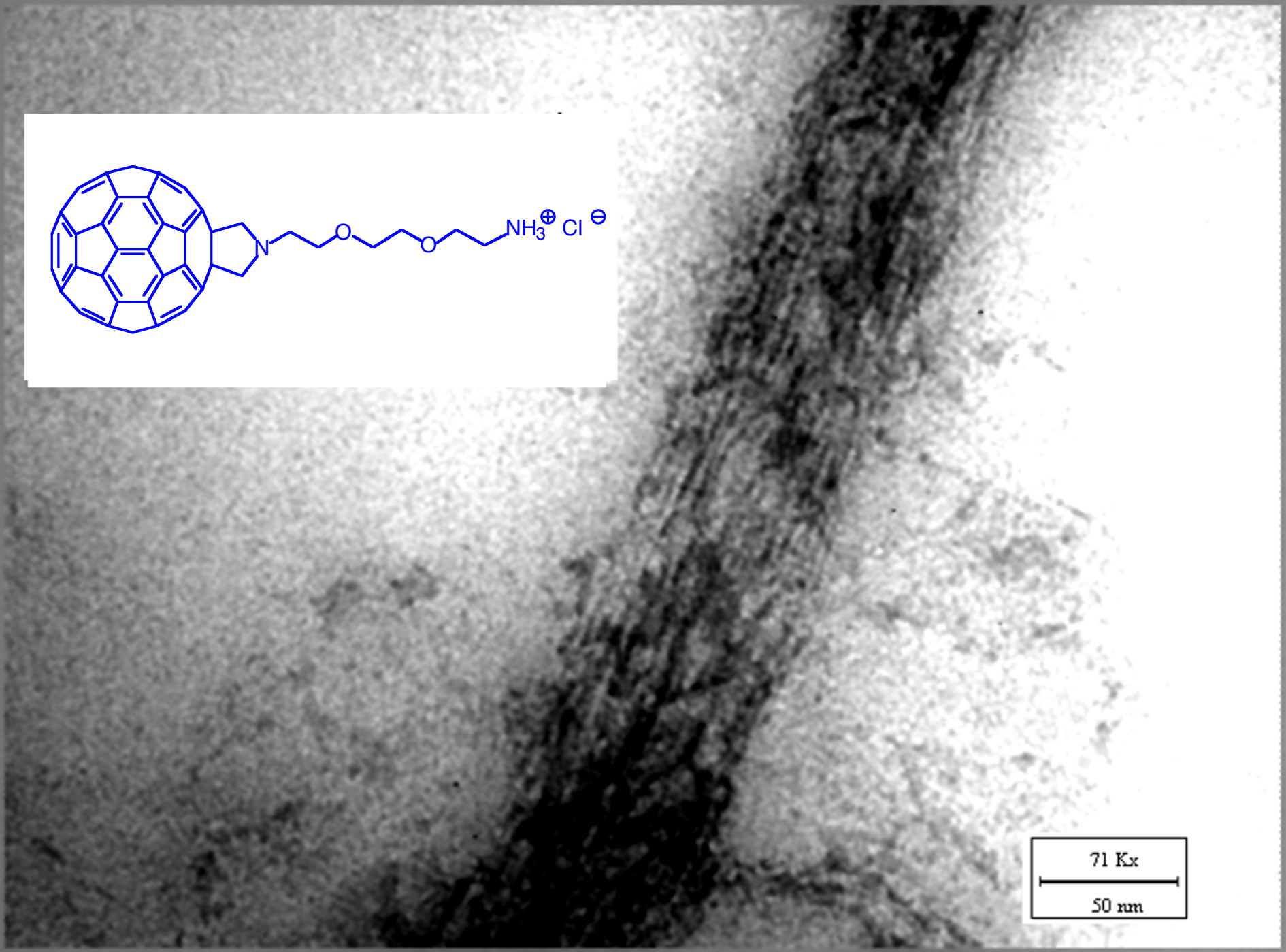


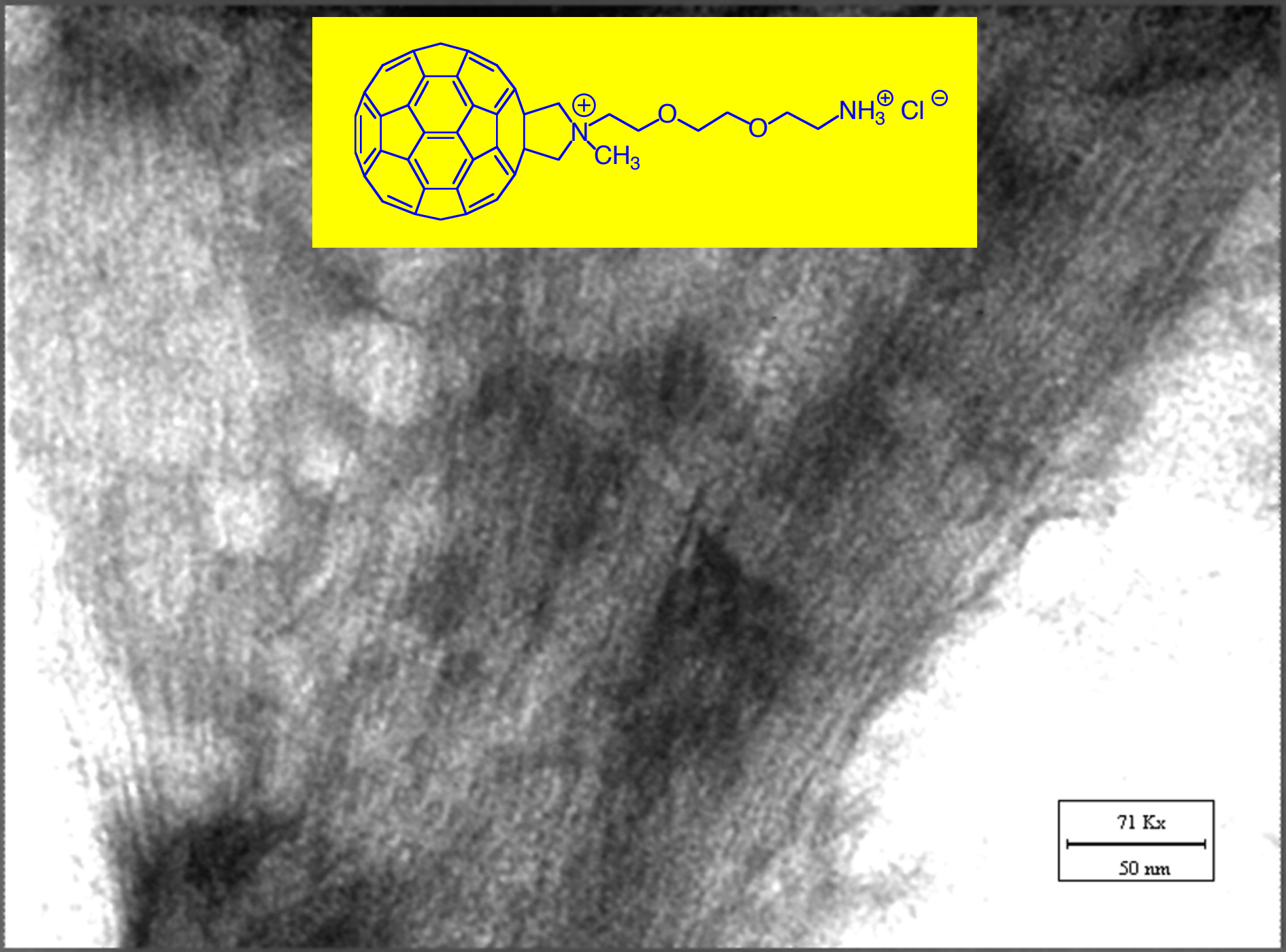

N
NH3 ⊕ Cl ⊖
1000 nm


NH3⊕ Cl⊖
N
600 nm

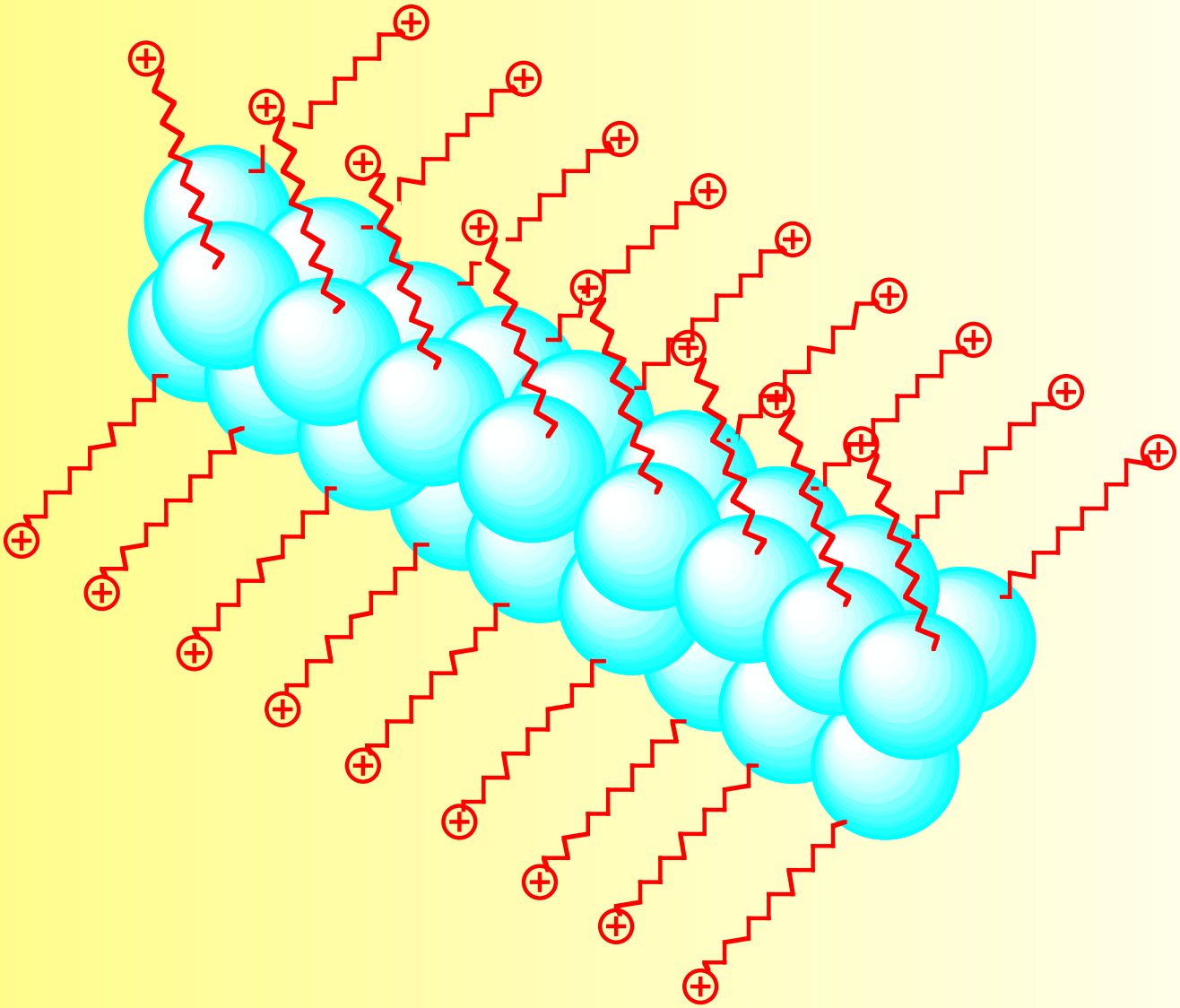
Do different fullerene structures lead to similar or different shapes of aggregation? Can the shapes be modeled?


N
O
O
NH3⊕ Cl⊖
1.4 Kx
1 µm


N
O
O
NH3⊕ Cl⊖
71 Kx
50 nm


O
O
NH3
Cl
CH3
71 Kx
50 nm

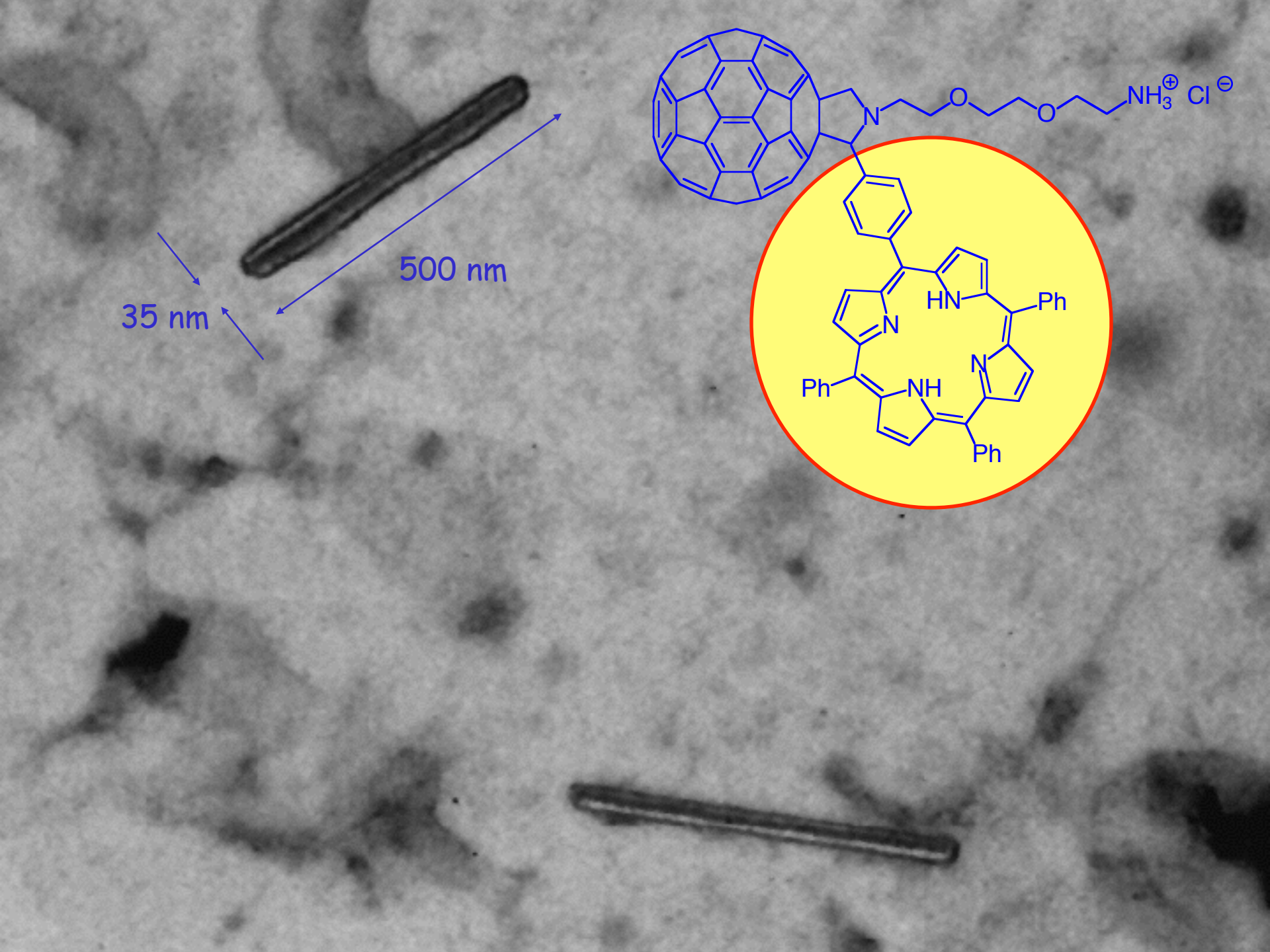
Self-Assembly is Driven by Fullerene Hydrophobicity

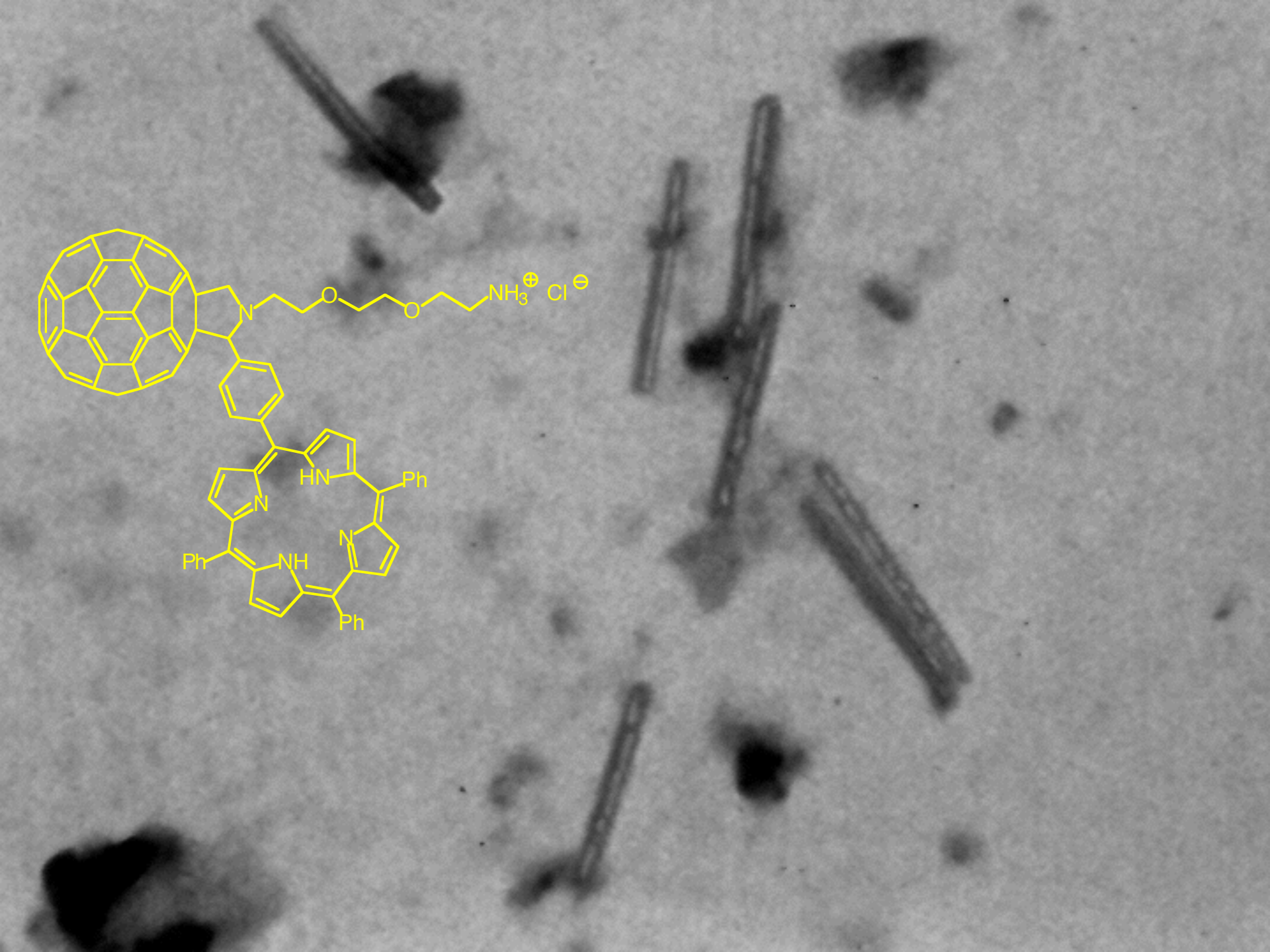


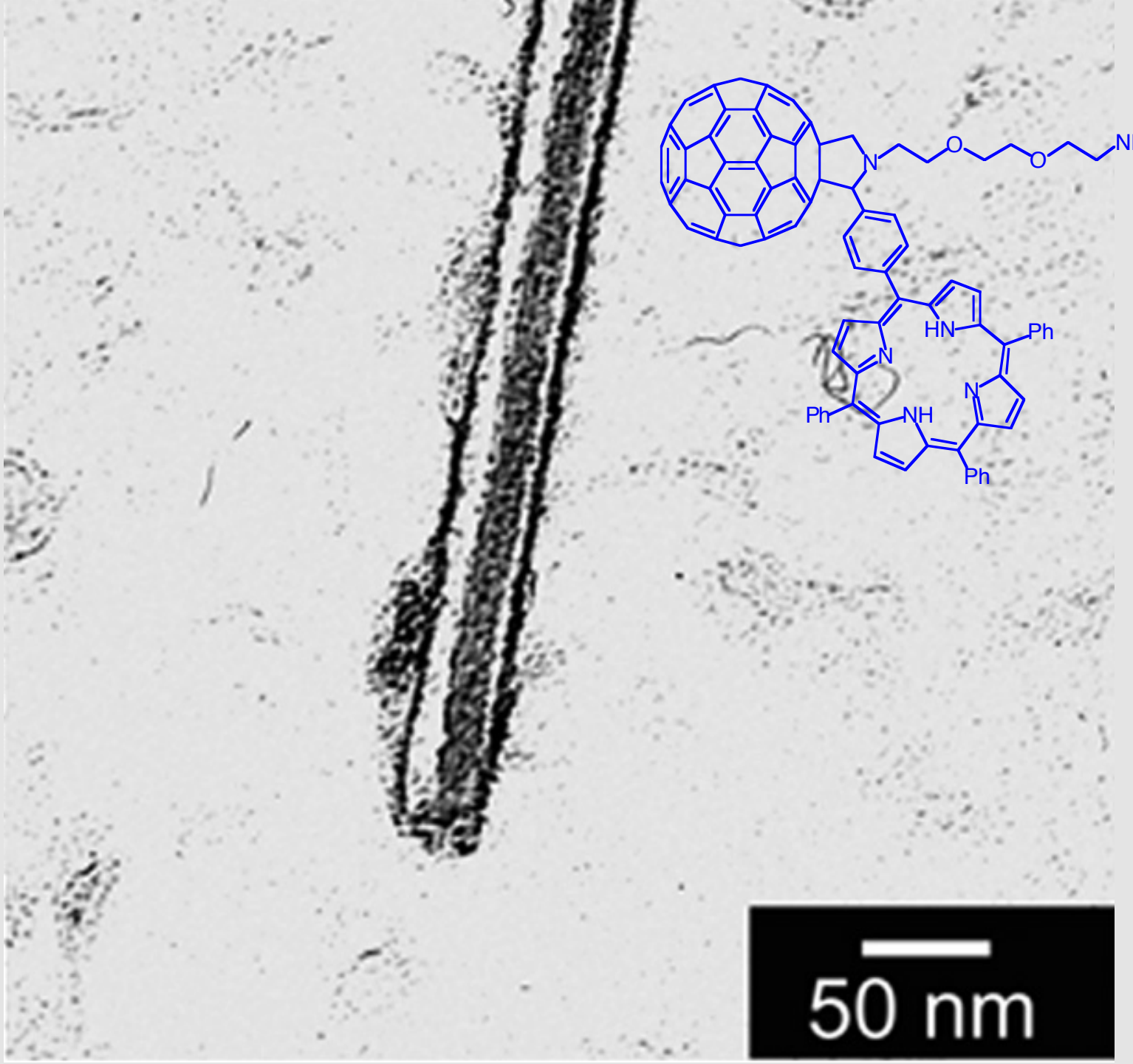
Can Perfection Be Achieved?

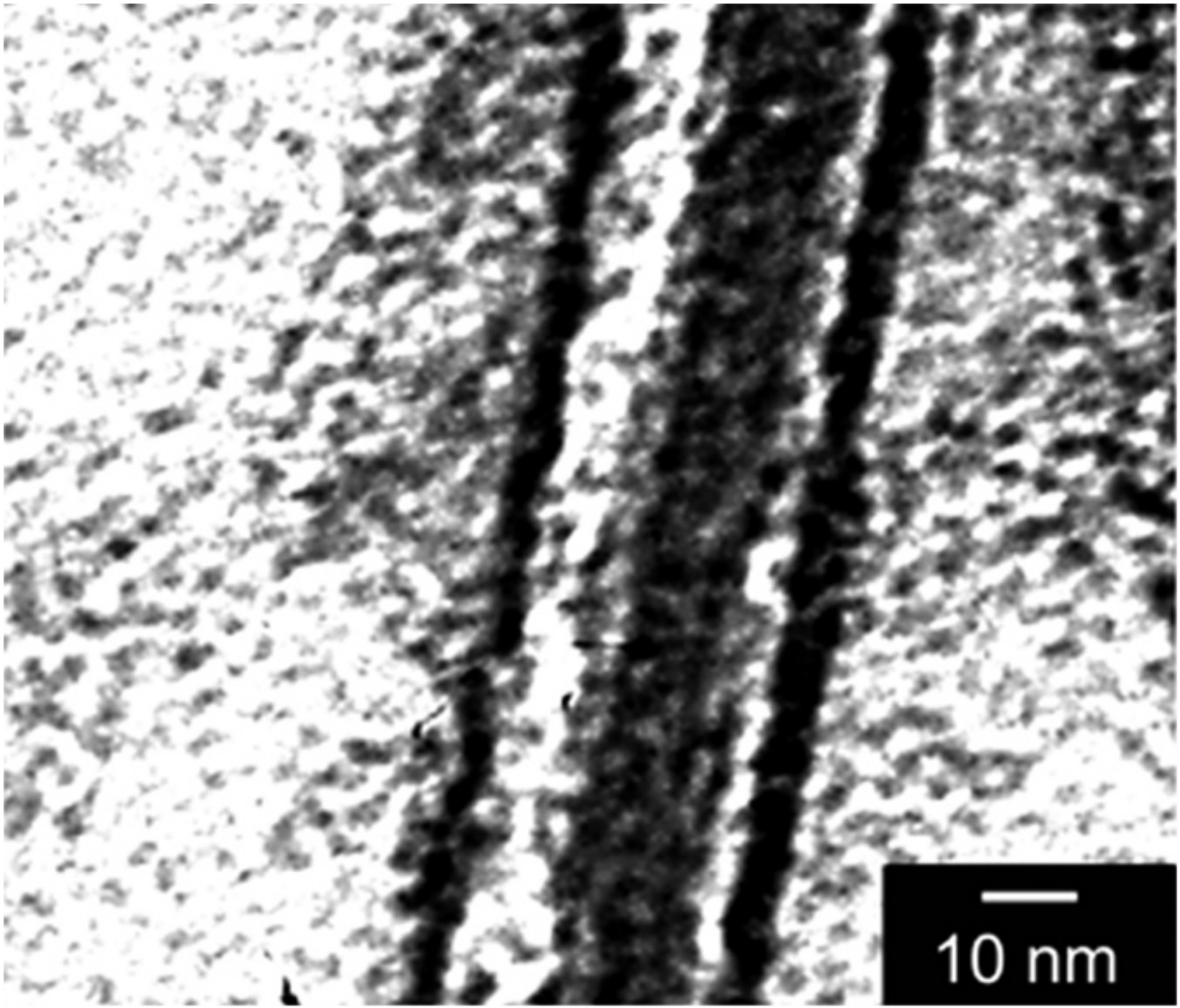
(perfectly structured nanoobjects
with defined structure, dimension and function)

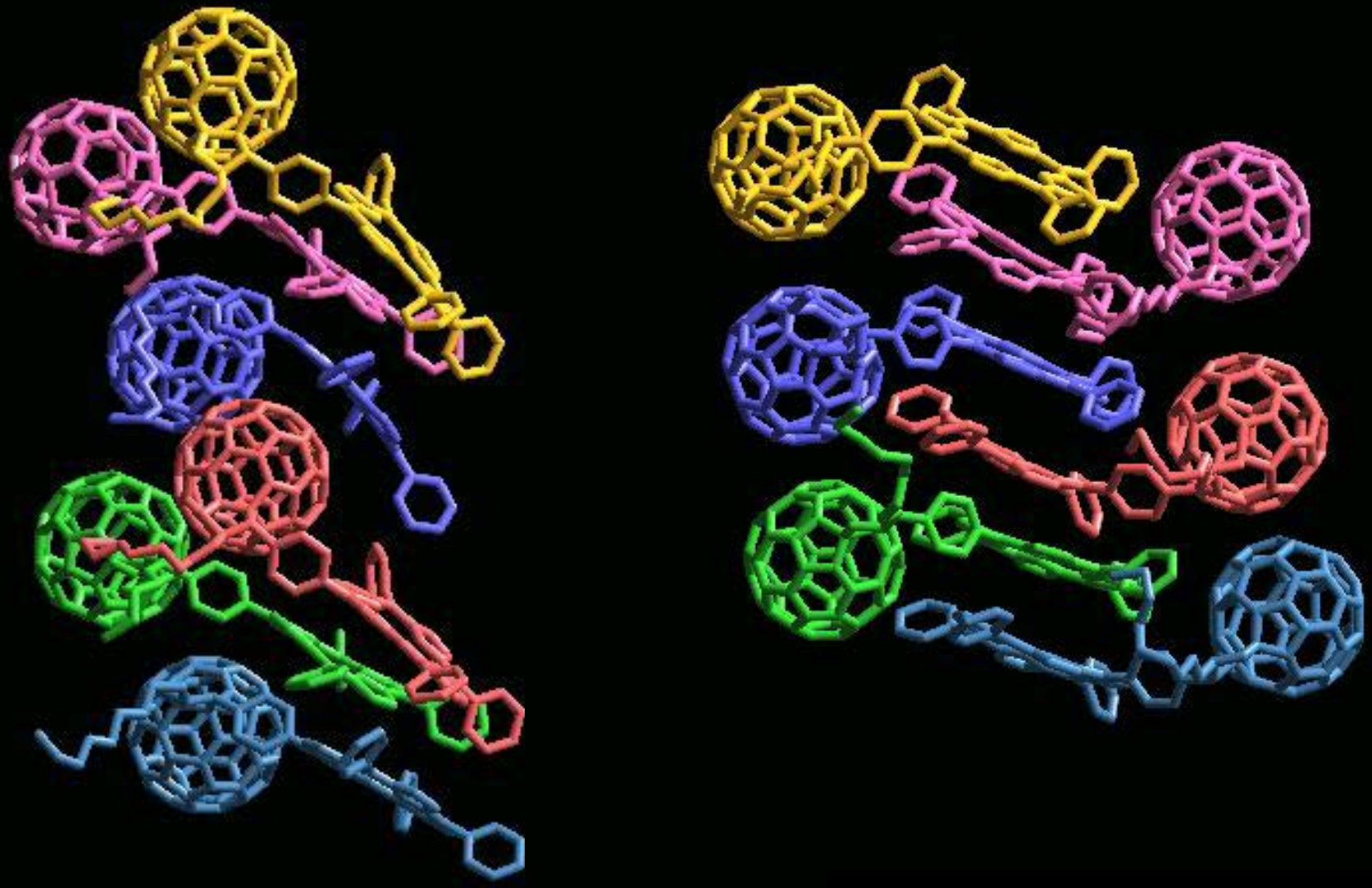
Maybe, but not with the systems studied so far
We need a further element of ordering


35 nm
500 nm
N
O
O
NH3 Cl
HN
Ph
N
N
Ph
NH
Ph

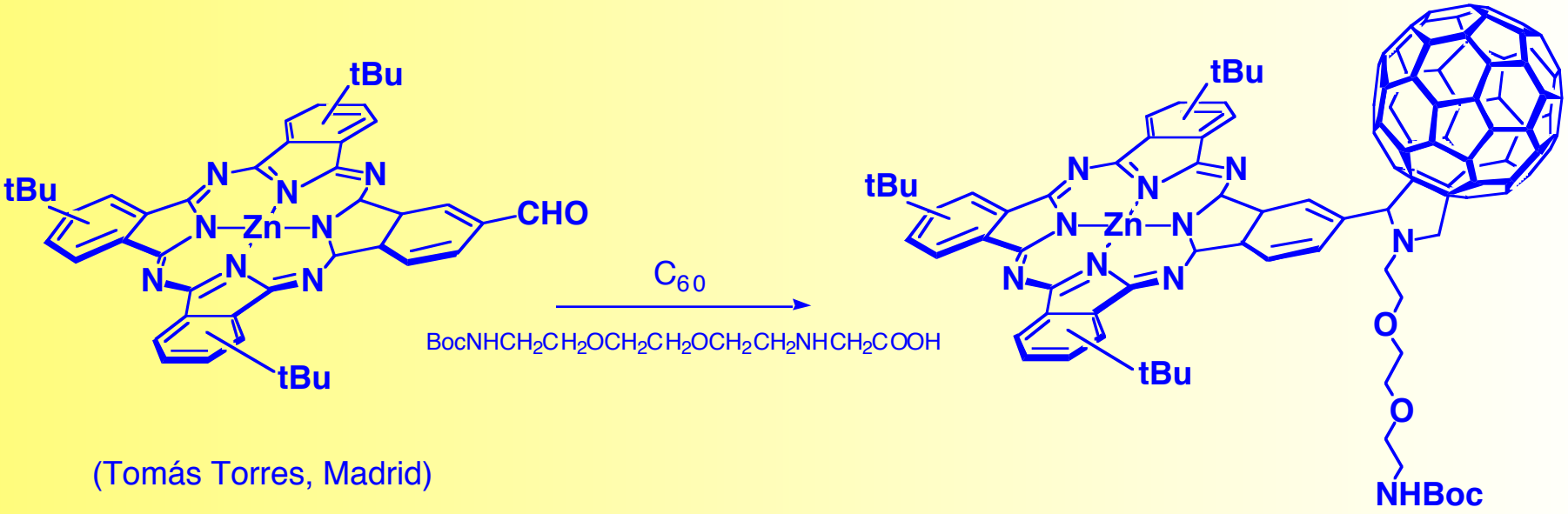

O
O
NH3
Cl
N
HN
Ph
N
N
Ph
NH
Ph


NH3 ⊕
Cl ⊖
O
O
N
HN
Ph
N
N
Ph
NH
Ph
50 nm

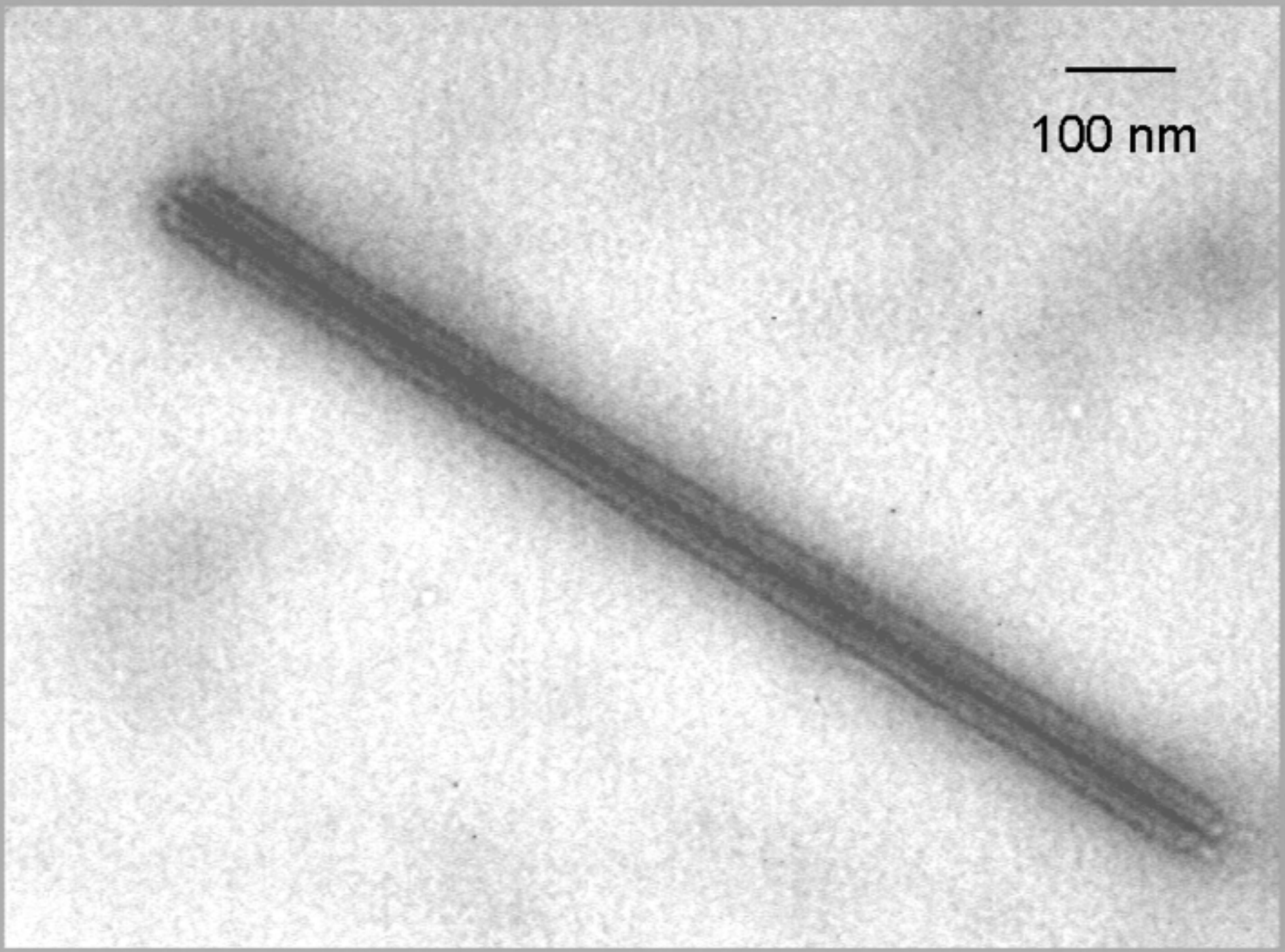

10 nm

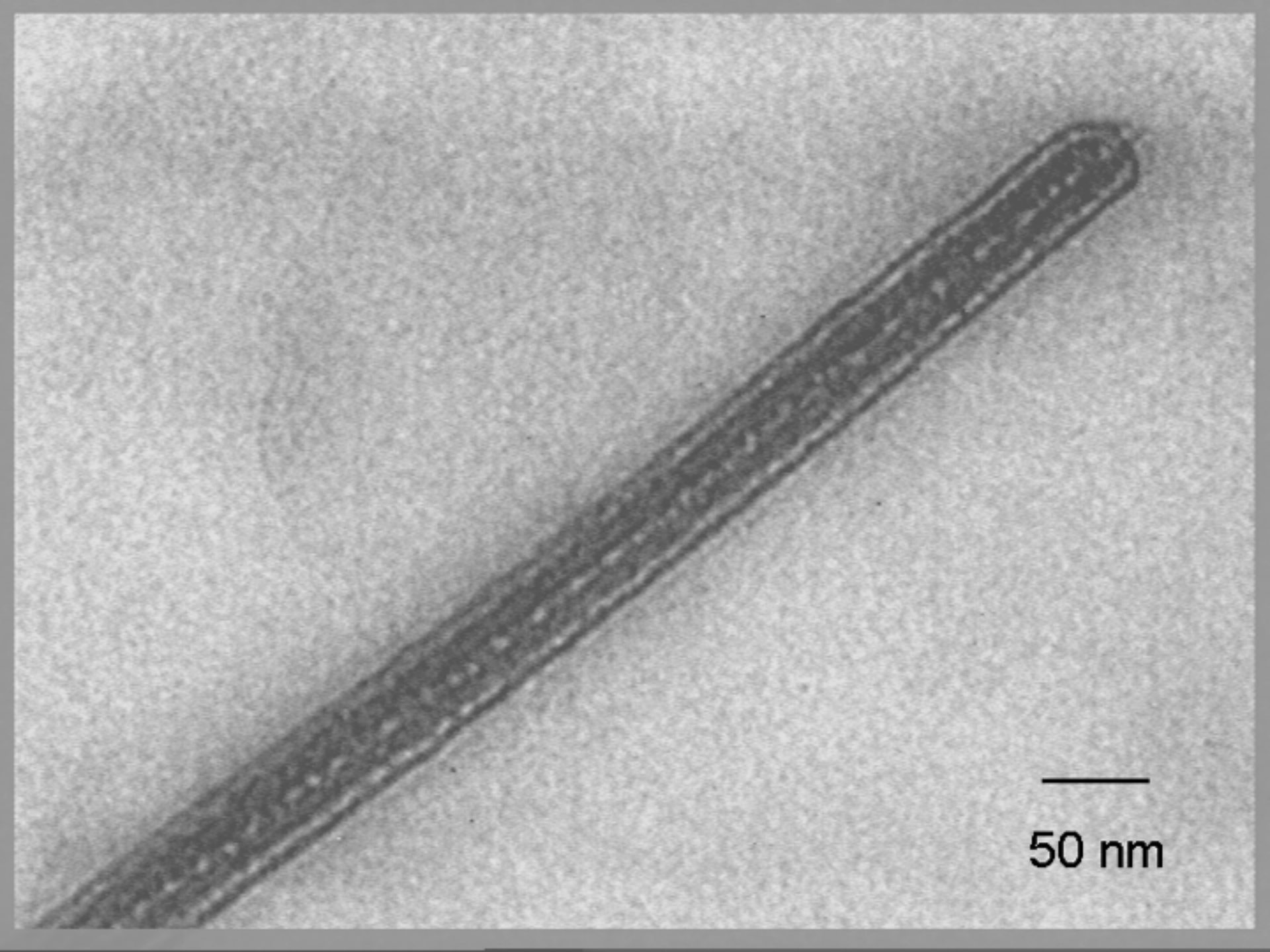


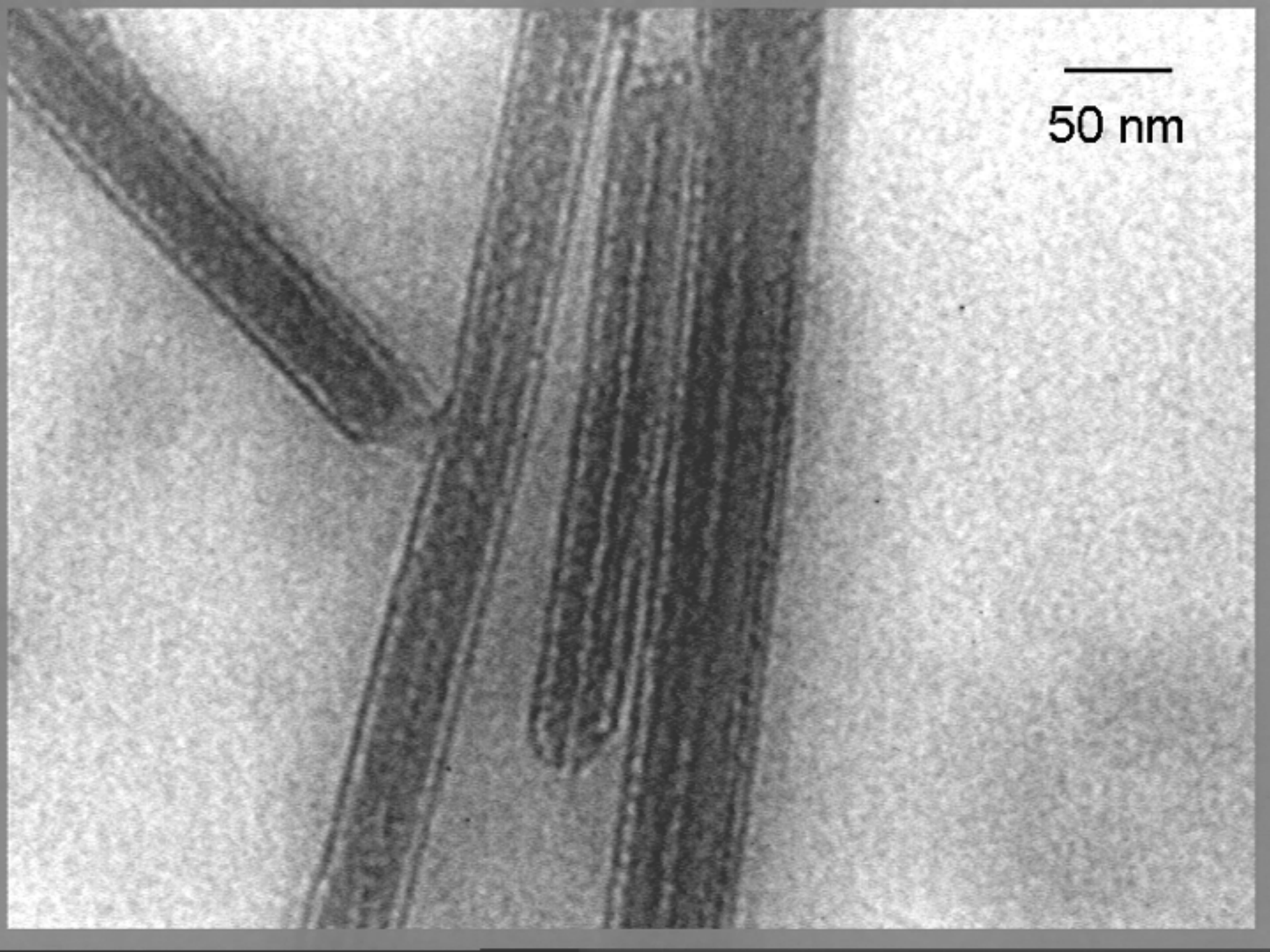
F. Zerbetto and M. Melle-Franco
(Tinker program)

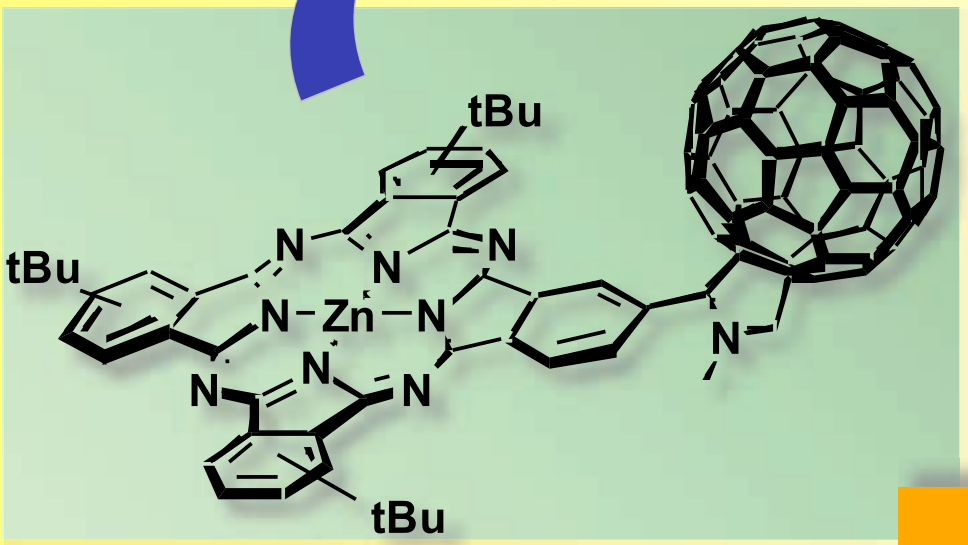


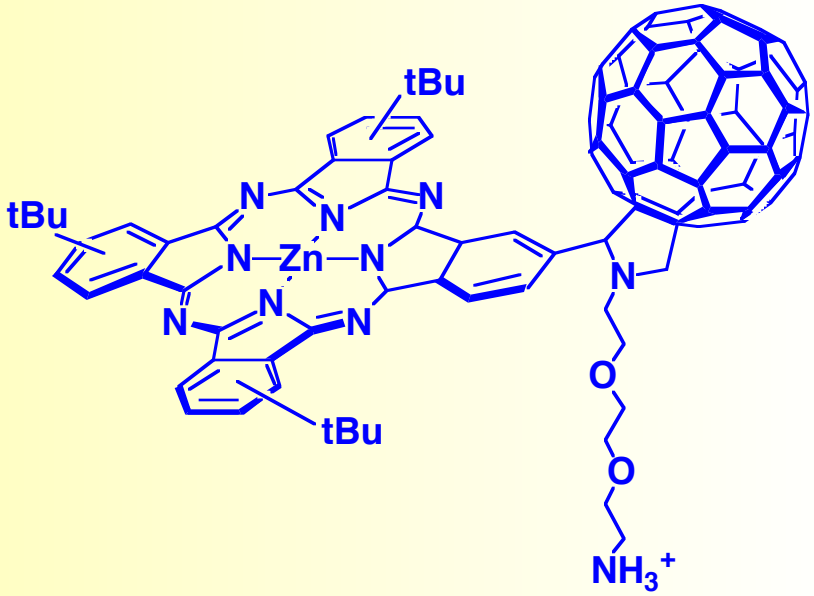
(Tomás Torres, Madrid)


100 nm


50 nm

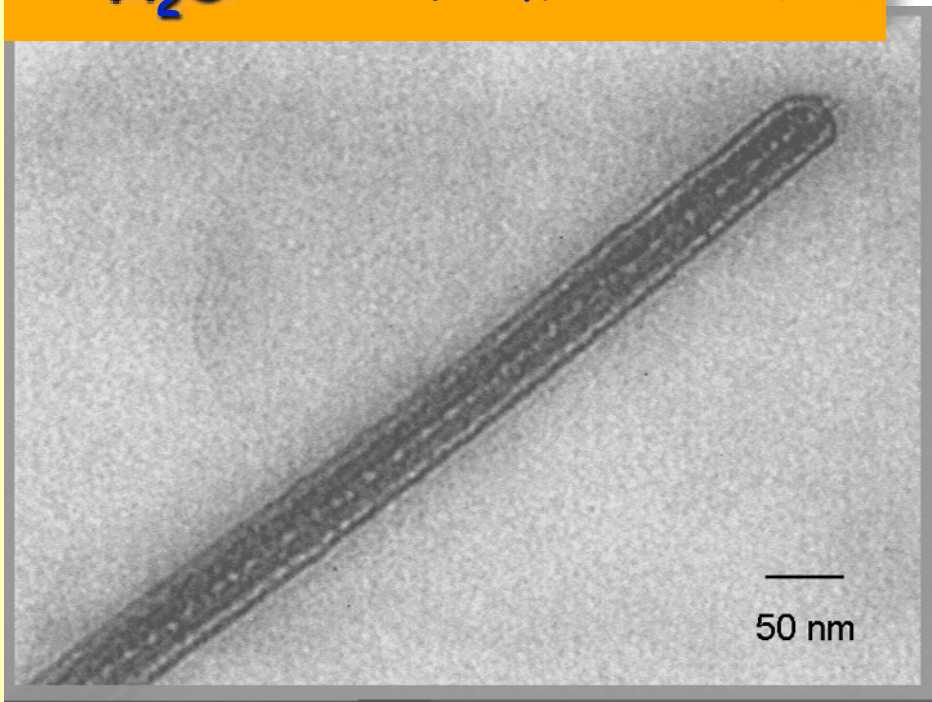

50 nm

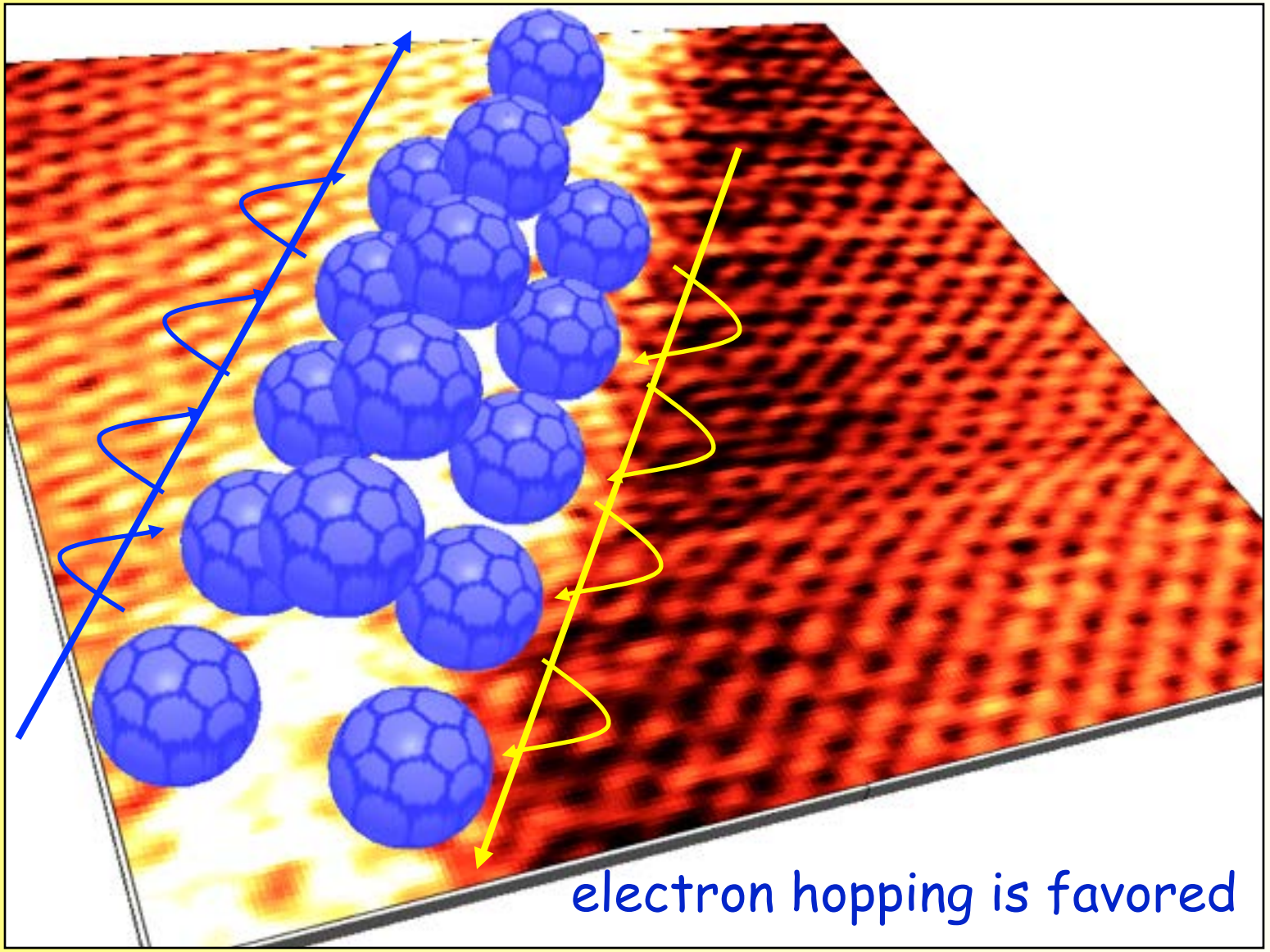




toluene	3.6 ns
chloroform	3.1 ns
o-DCB	2.7 ns
benzonitrile	2.3 ns

H_2O 1.4 milliseconds!




electron hopping is favored

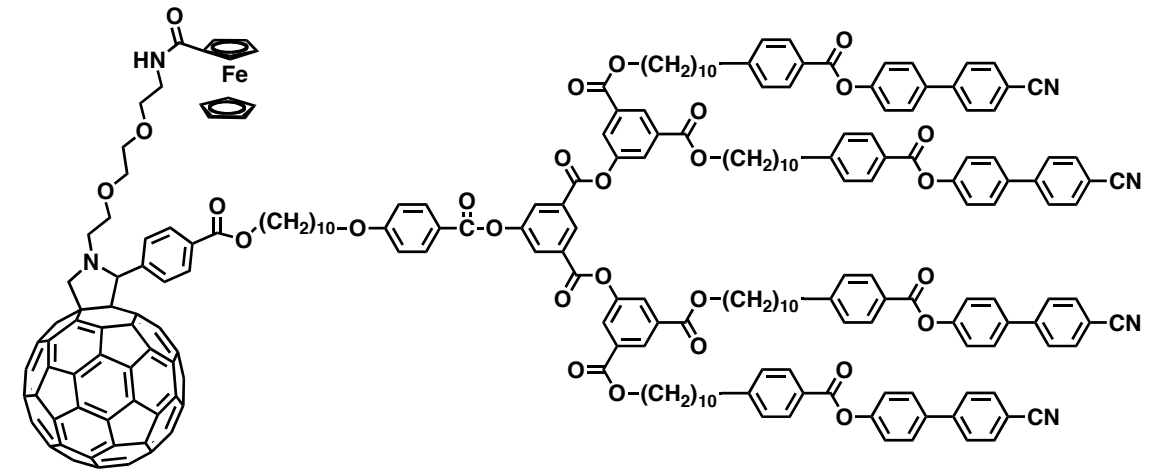
CONCLUSIONS

1) Short alkyl chains seem to favor spherical micelle-type of aggregation

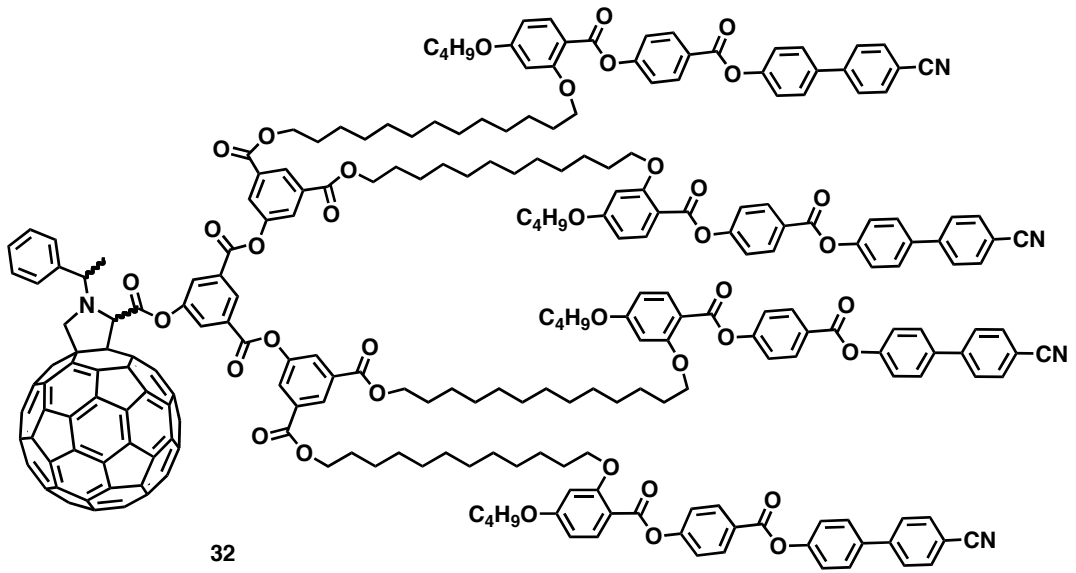
2) Long hydrophilic chains seem to favor long rod-type of aggregation

3) Addition of templating systems such as porphyrins or phthalocyanines leads to nanoobjects with well defined structures

4) The self-assembly process can favor the formation of C_{60} networks useful for nanotechnological applications



31



32

(R,S) (S, R) (R,R) (S,S)

J. Mater. Chem., 2004, **14**, 1266

Optical limiters are important for protection of optical sensors or human eyes against damage from high-energy laser light

- Laser medicine
- Military Industry
- Electronic Industry

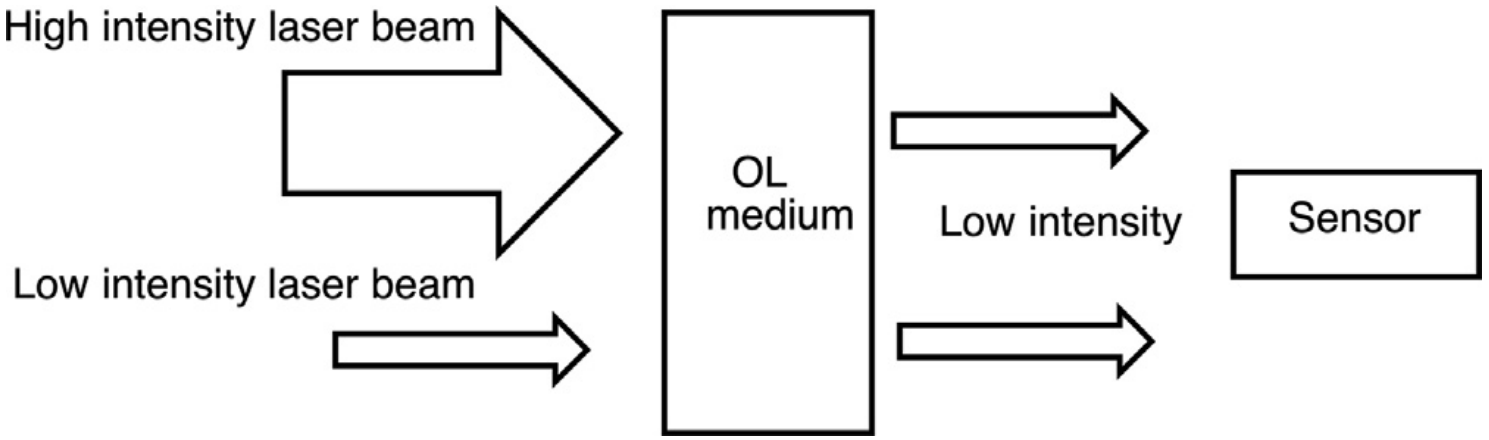


Fig. 1. Passive optical limiting for sensor protection with different laser intensities.

the optical limiting performance depends on the pulse width of laser, nature of the solvent, solution concentration (and carbon black particle size). As the formation of scattering centers (microplasmas and bubbles) occurs over a period of several nanoseconds, CBS is the most effective for a laser pulse longer than nanoseconds.

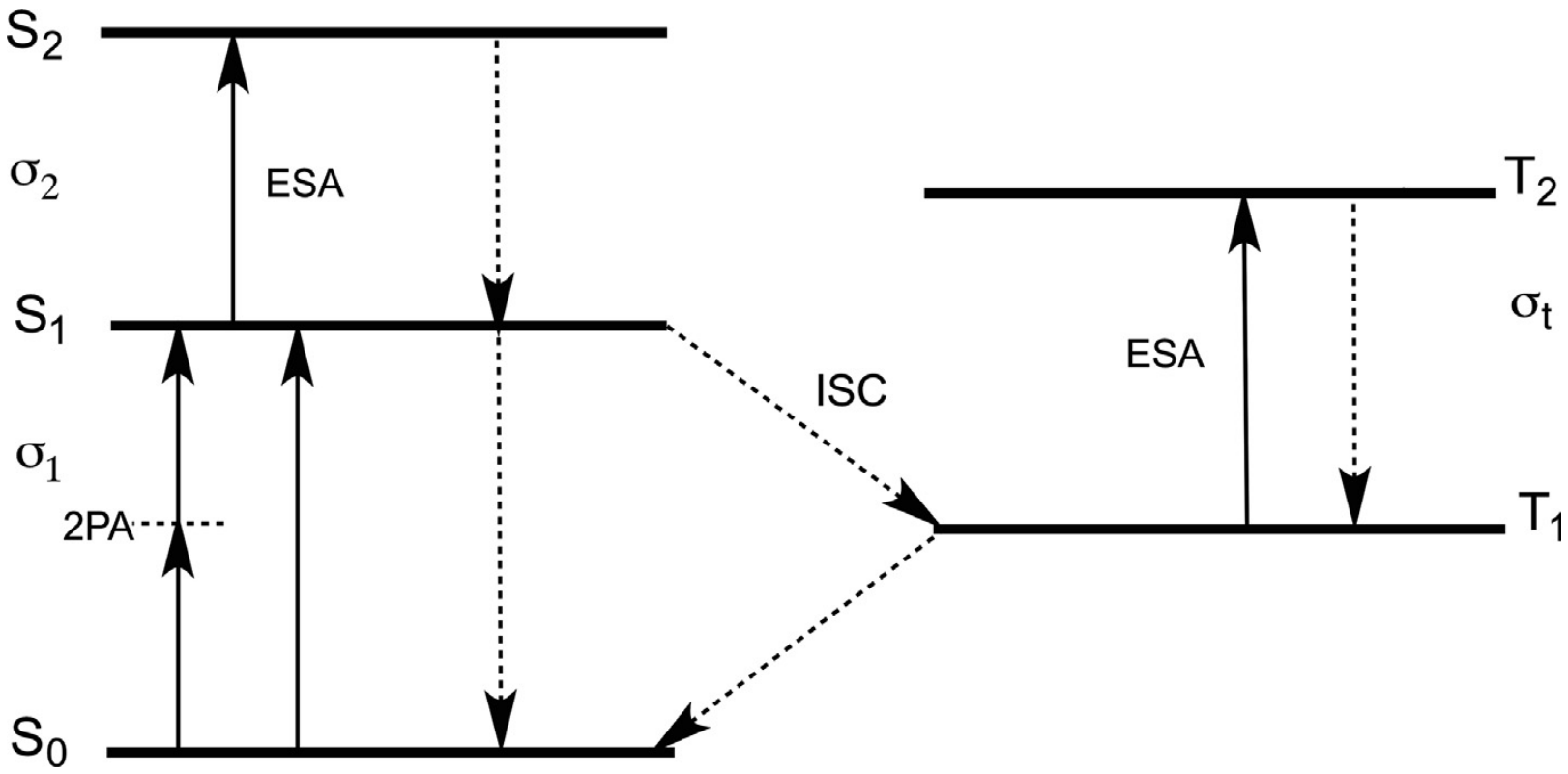
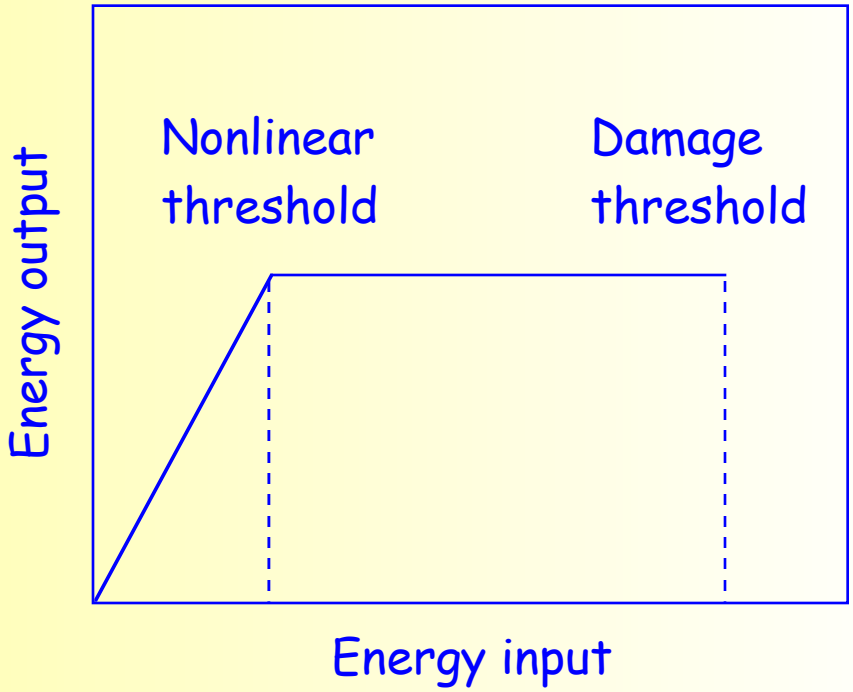


Fig. 3. Five-level Jablonski diagram showing some NLA effects.

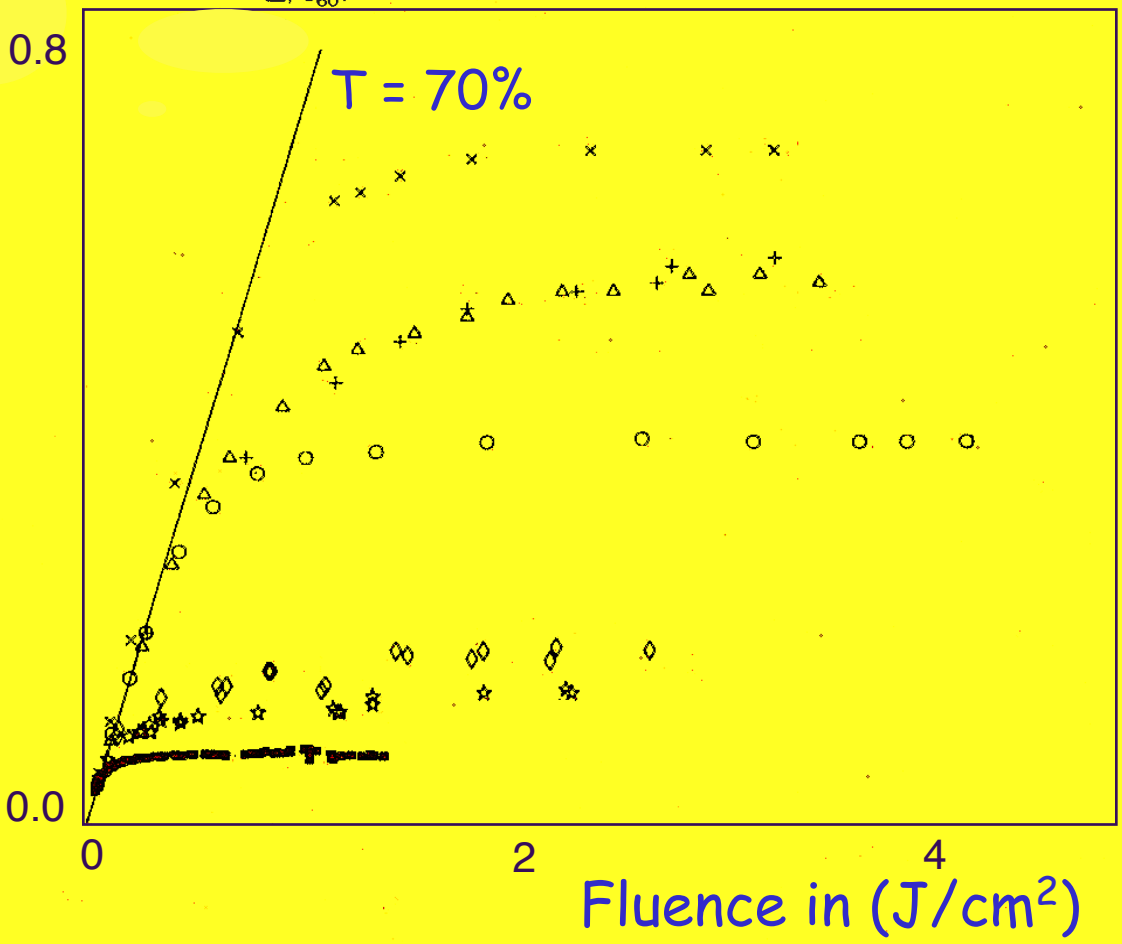
Important features of an OL device

- high linear transmission for low input levels
- large dynamic range (wide absorption window)
- low threshold for nonlinear transmission



Comparison of the Optical Limiting Response of C_{60} with other optical limiters (Tutt & Kost, Nature 1992)

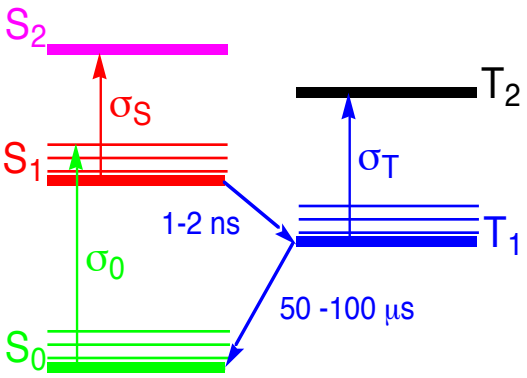
FIG. 2 Comparison of the optical limiting response of solutions of various reported optical limiters to C_{60} in toluene. All comparison solutions are 70% transmitting at 532 nm, and the solvent was methylene chloride, except with the two exceptions of chloroaluminum phthalocyanine, which was dissoved in methanol, and indanthrone, dissolved in dilute KOH. ○, $HFeCo_3(CO)_{10}(P(CH_3)_3)_2$; △, $HFeCo_3(CO)_{12}$; +, $(N(C_2H_5)_4)^+(FeCo_3(CO)_{12})^-$; ×, $HFeCo_3(CO_{10})(P\,Ph_3)_2$; ◇, indanthrone; ☆, chloroaluminium phthalocyanine; ■, C_{60}.

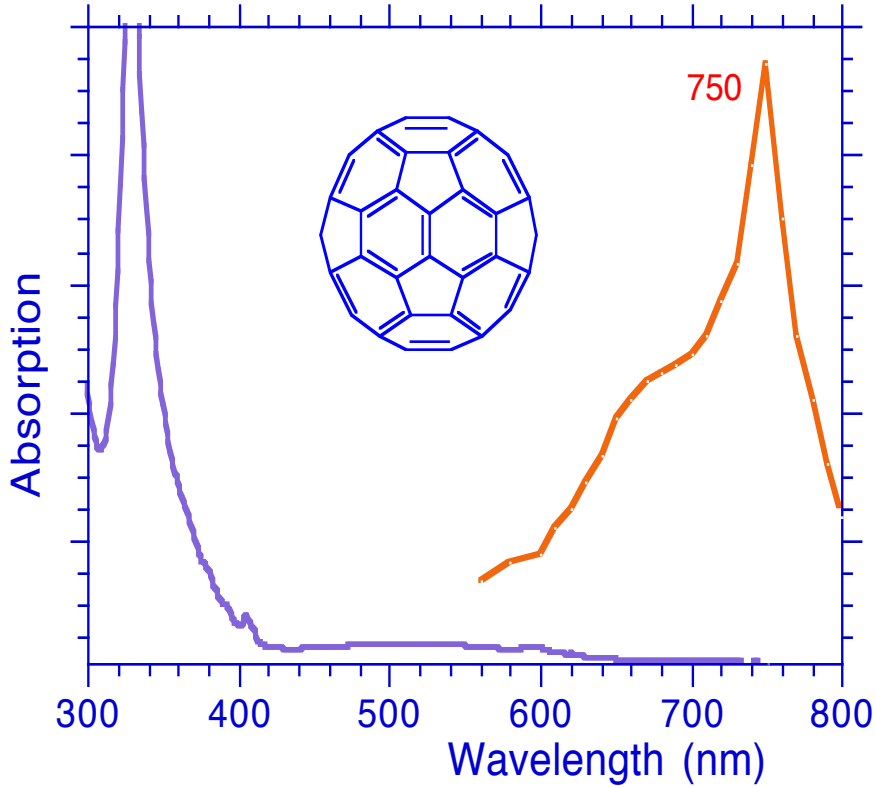


Ground State and First Triplet Excited State Absorptions in Unmodified C_{60}

$$\Phi \geq 0.96$$

$$\frac{\sigma_T \propto (\varepsilon_T)}{\sigma_0 \propto (\varepsilon_0)} \gg 1$$





Reverse Saturable Absorption
- efficient pumping to the excited state
- strongly absorbing excited state

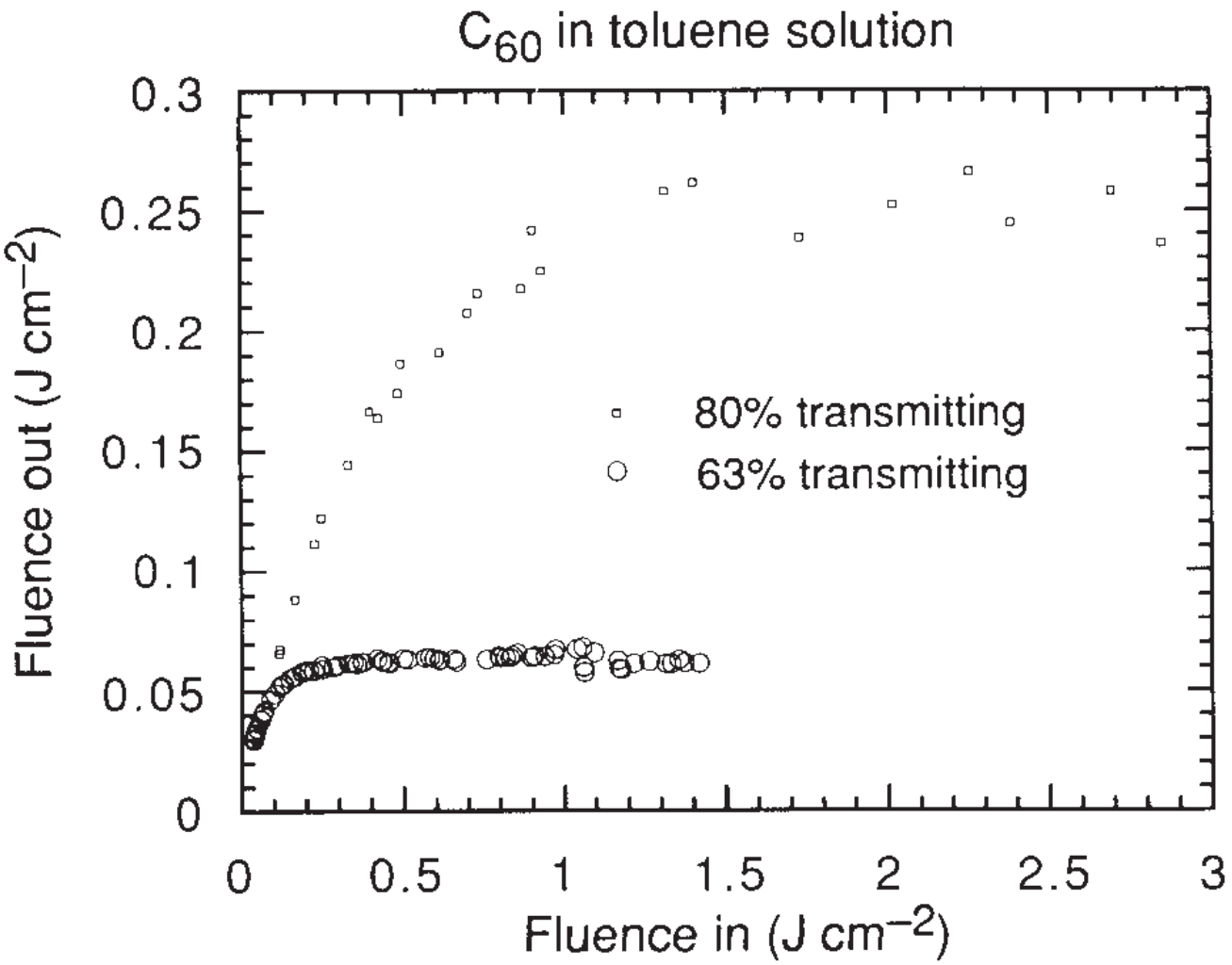
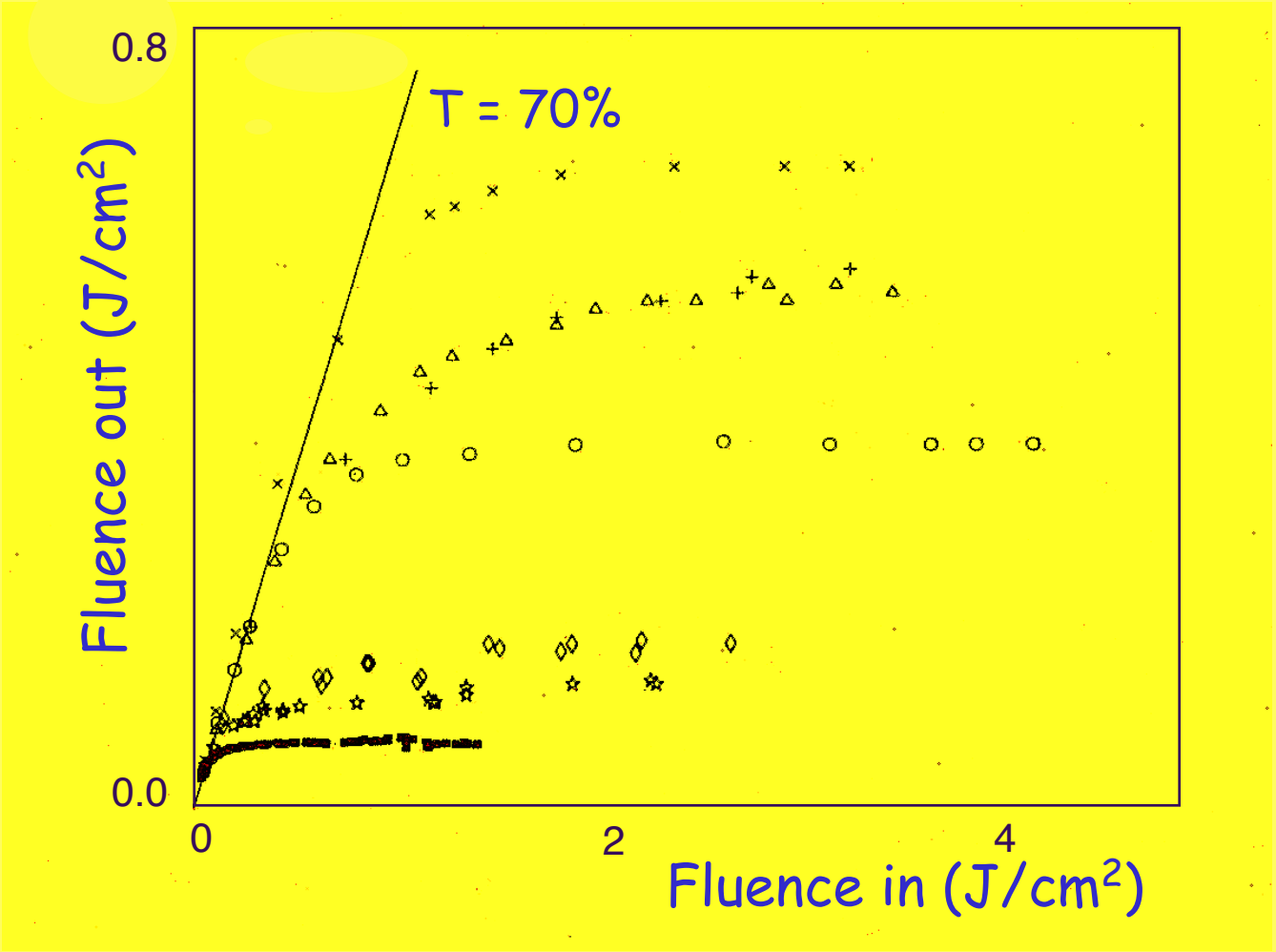
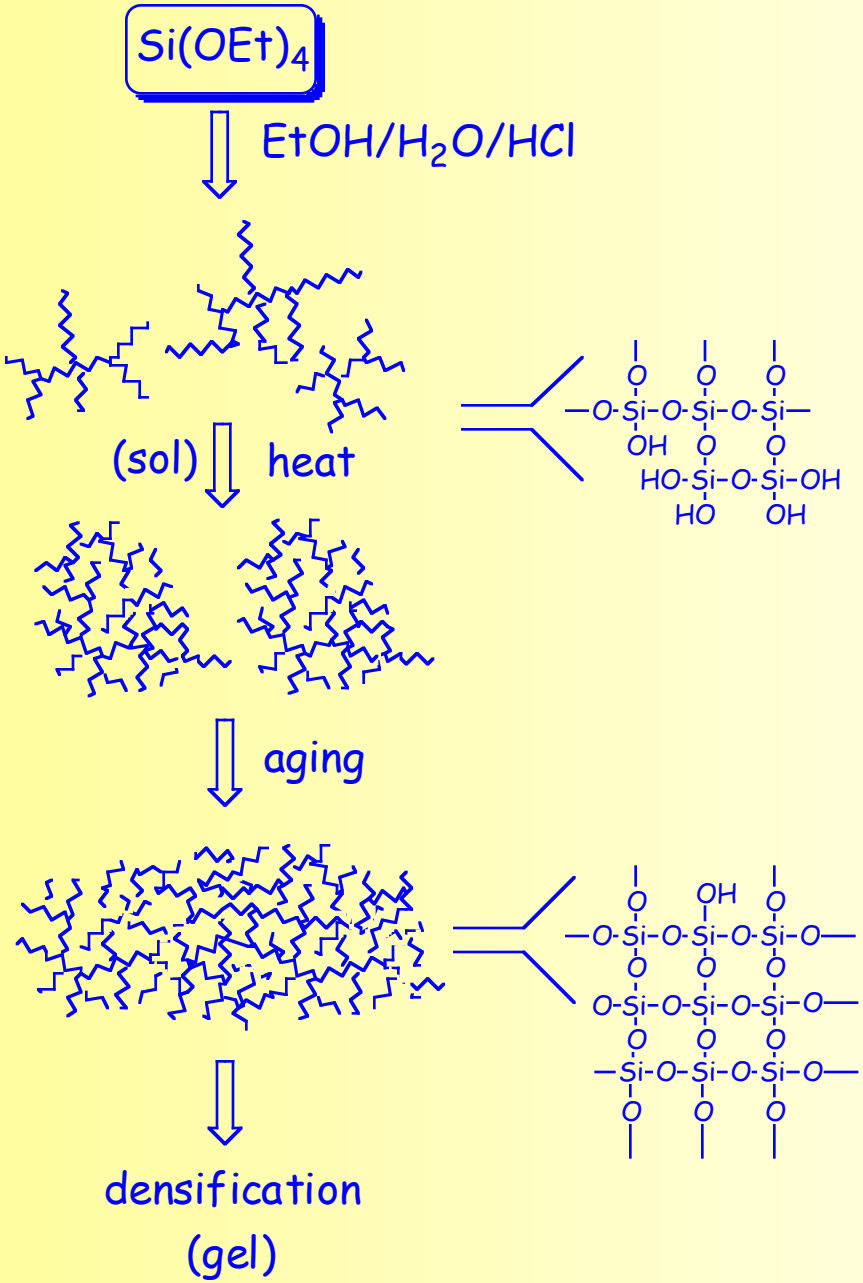


FIG. 1 Optical limiting response of 63% and 80% transmitting solutions of C_{60} in toluene to 7 ns, 532 nm optical pulses.

Comparison of the Optical Limiting Response of C_{60} with other optical limiters (Tutt & Kost, Nature 1992)

TOLUENE SOLUTION, 532 nm



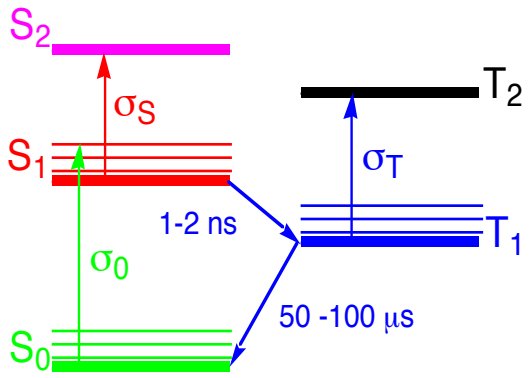

Si(OEt)4
EtOH/H2O/HCl
(sol)
heat
aging
densification
(gel)

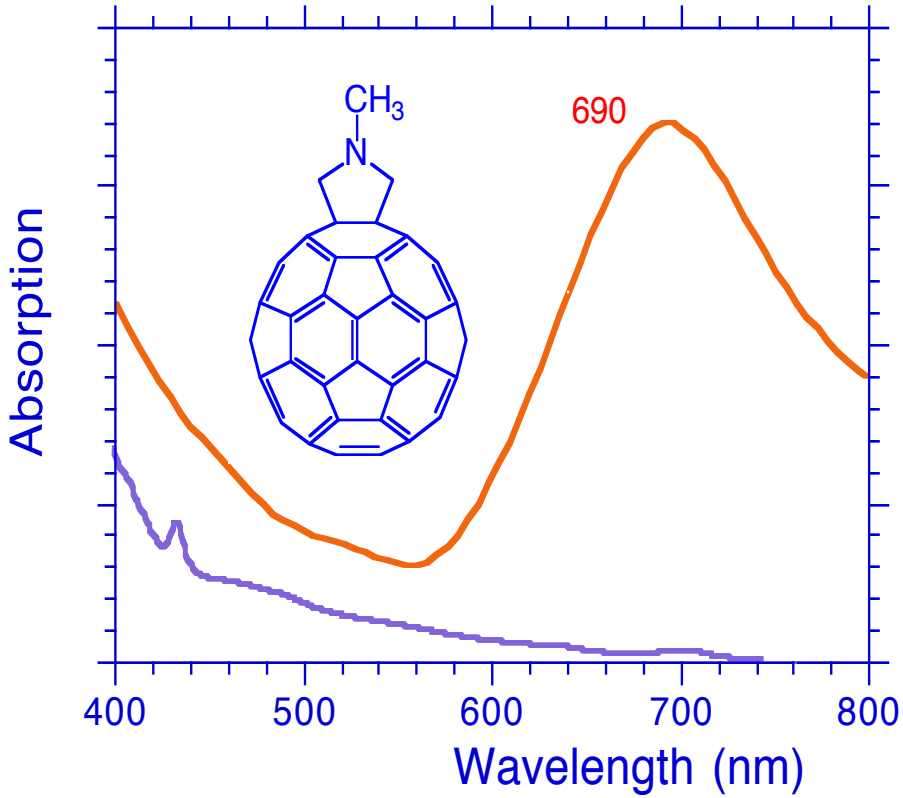
C_{60} - Containing Sol-Gel Slabs

Ground State and First Triplet Excited State Absorptions in N-Methyl-Pyrrolidine

$$\Phi \geq 0.90$$

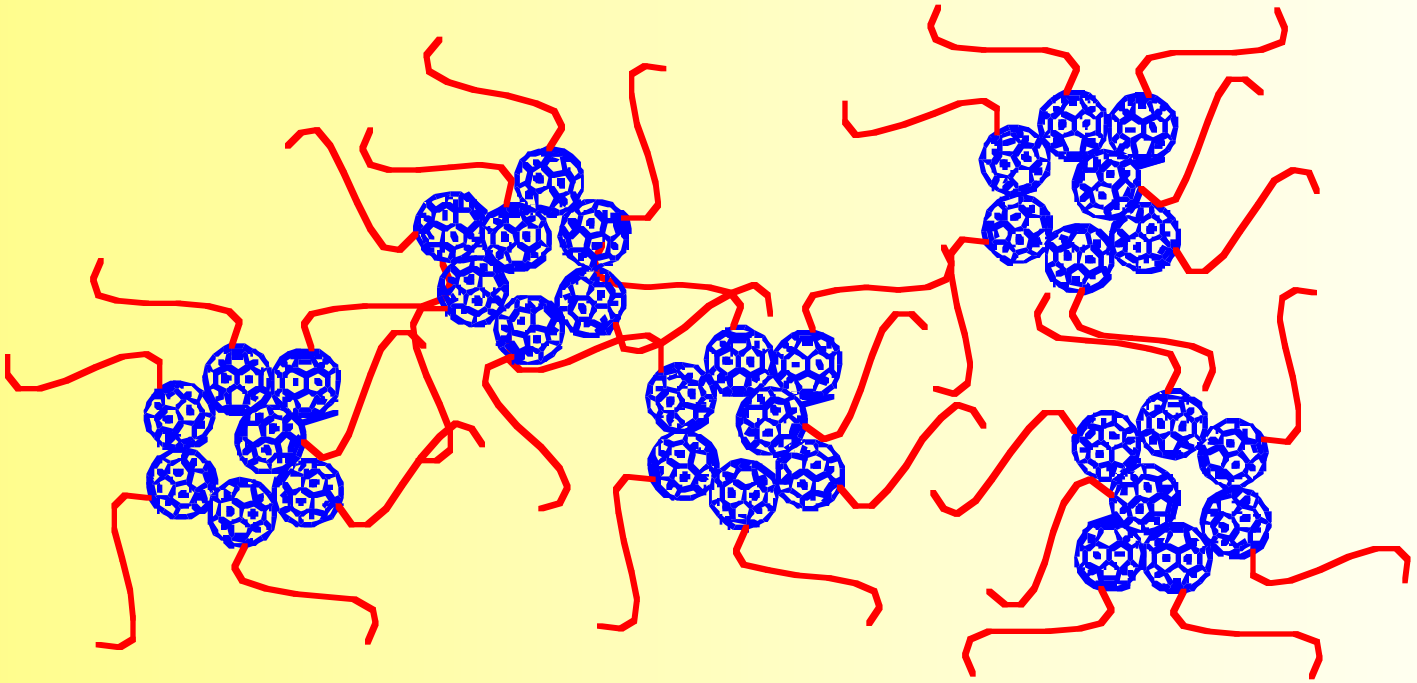
$$\frac{\sigma_T \propto (\varepsilon_T)}{\sigma_0 \propto (\varepsilon_0)} \gg 1$$





Acc. Chem. Res. **2000**, 33, 695-703

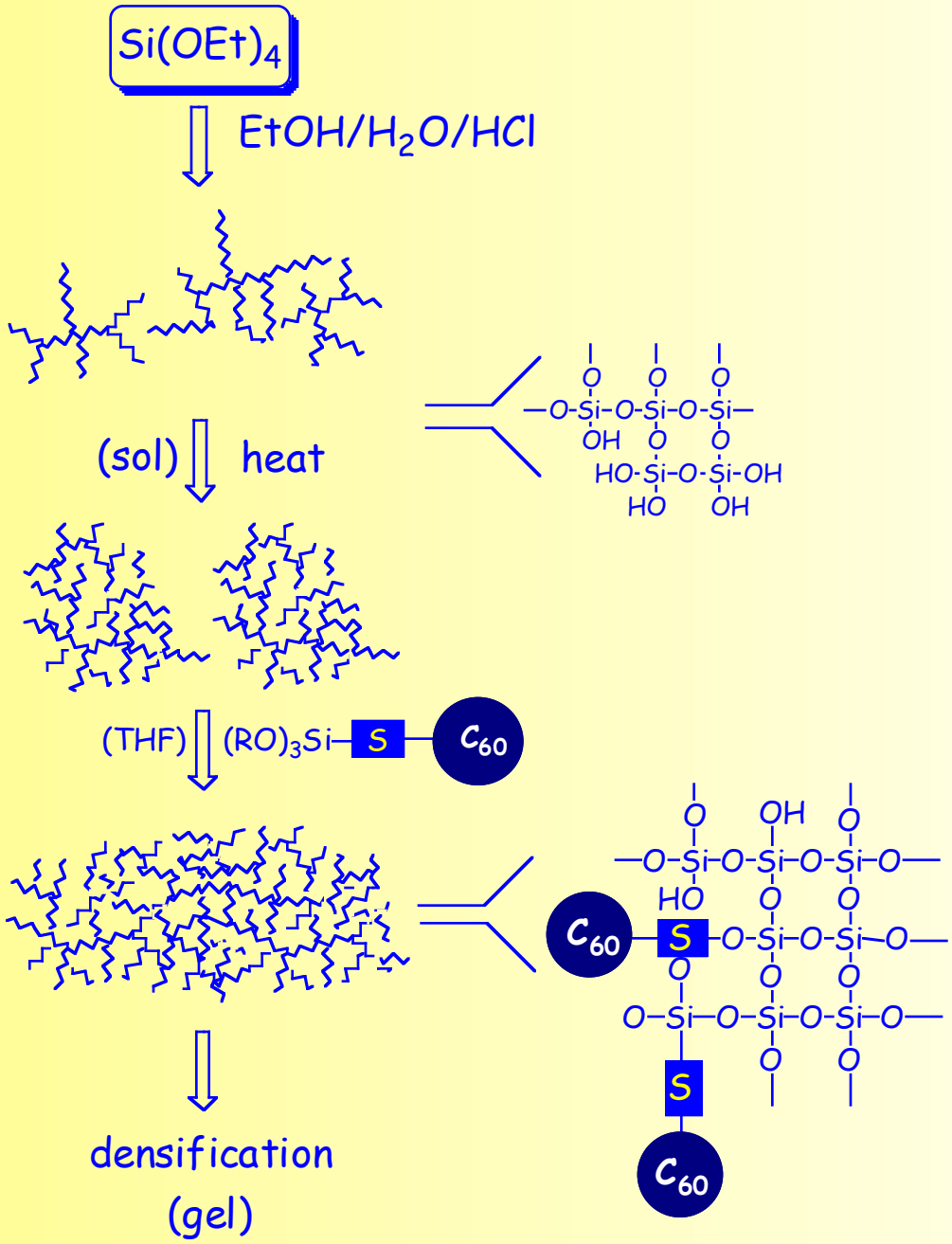
Triplet lifetimes decrease by 2-3 orders of magnitude in solution and in the solid state



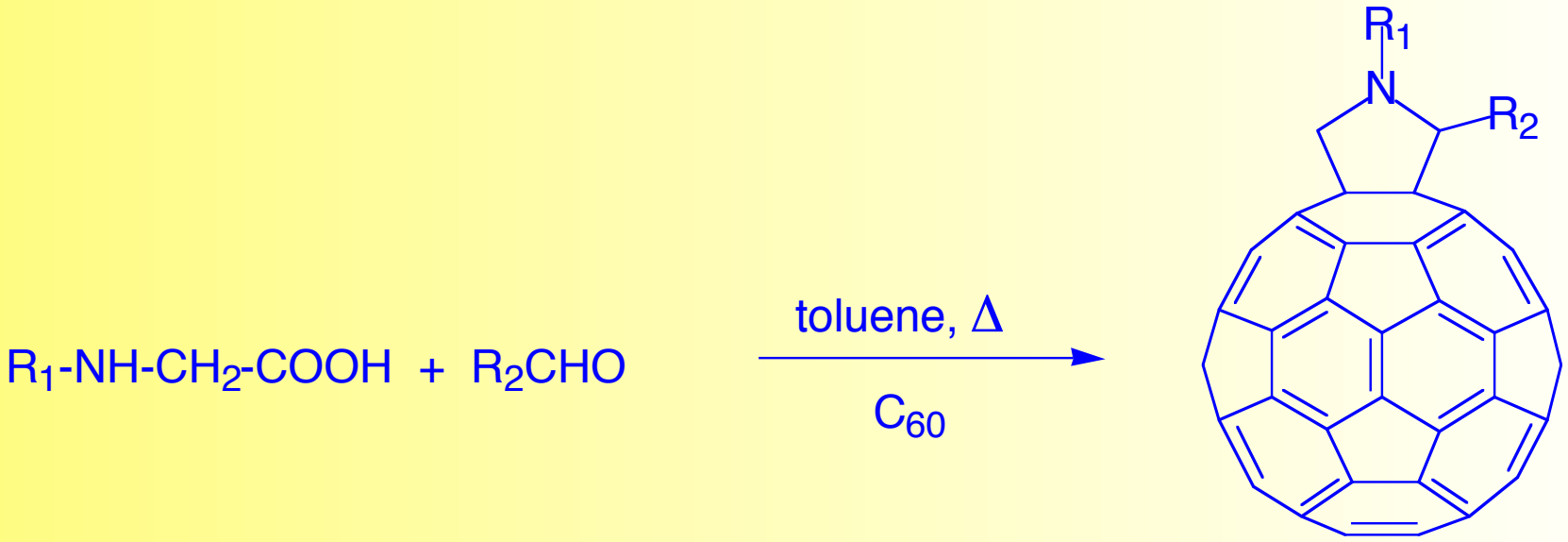
Solution: J. Eastoe, E. Crooks, A. Beeby and R. Heenan, Chem. Phys. Lett., 1995, 245, 571; D. M. Guldi, J. Phys. Chem. A, 1997, 101, 3895.

Sol-gel glasses: D. W. McBranch, V. Klimov, L. B. Smilowitz, M. Grigorova, J. M. Robinson, A. Koskelo, B. R. Mattes, H. Wang and F. Wudl in Fullerenes and Photonics III, Ed. Z. H. Kafafi, SPIE, Bellingham, 1996, 140

Review: D. Guldi and M. Prato, Acc. Chem. Res. 2000, 33, 695.


Si(OEt)4
EtOH/H2O/HCl
(sol)
heat
(THF)
(RO)3Si
S
C60
densification
(gel)

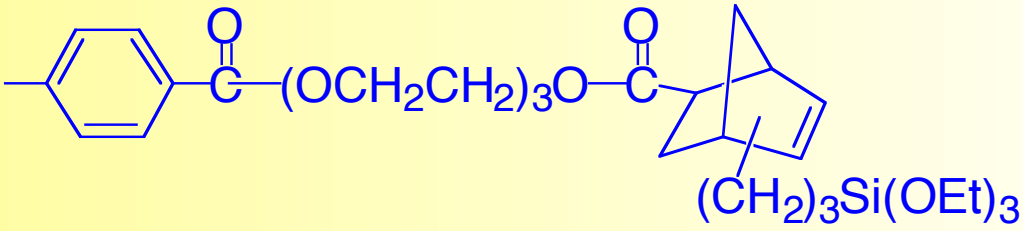
Synthesis of Silicon-Alkoxide Functionalized Fullerenes



R_1 = —$(CH_2CH_2O)_3CH_3$, R_2 = —$(CH_2)_{10}Si(OMe)_3$

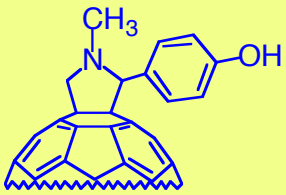
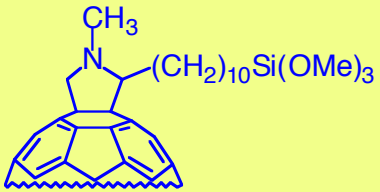
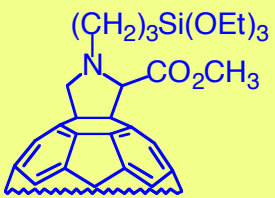
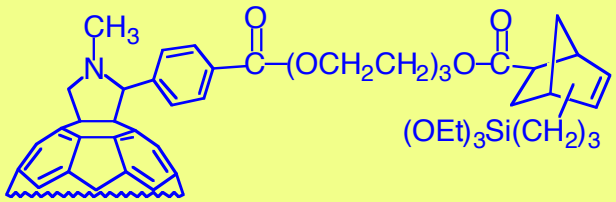
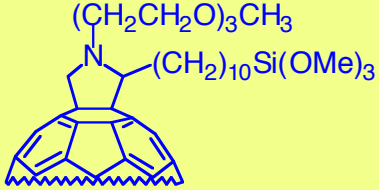
R_1 = —CH_3, R_2 = —$(CH_2)_{10}Si(OMe)_3$

R_1 = —CH_3, R_2 =

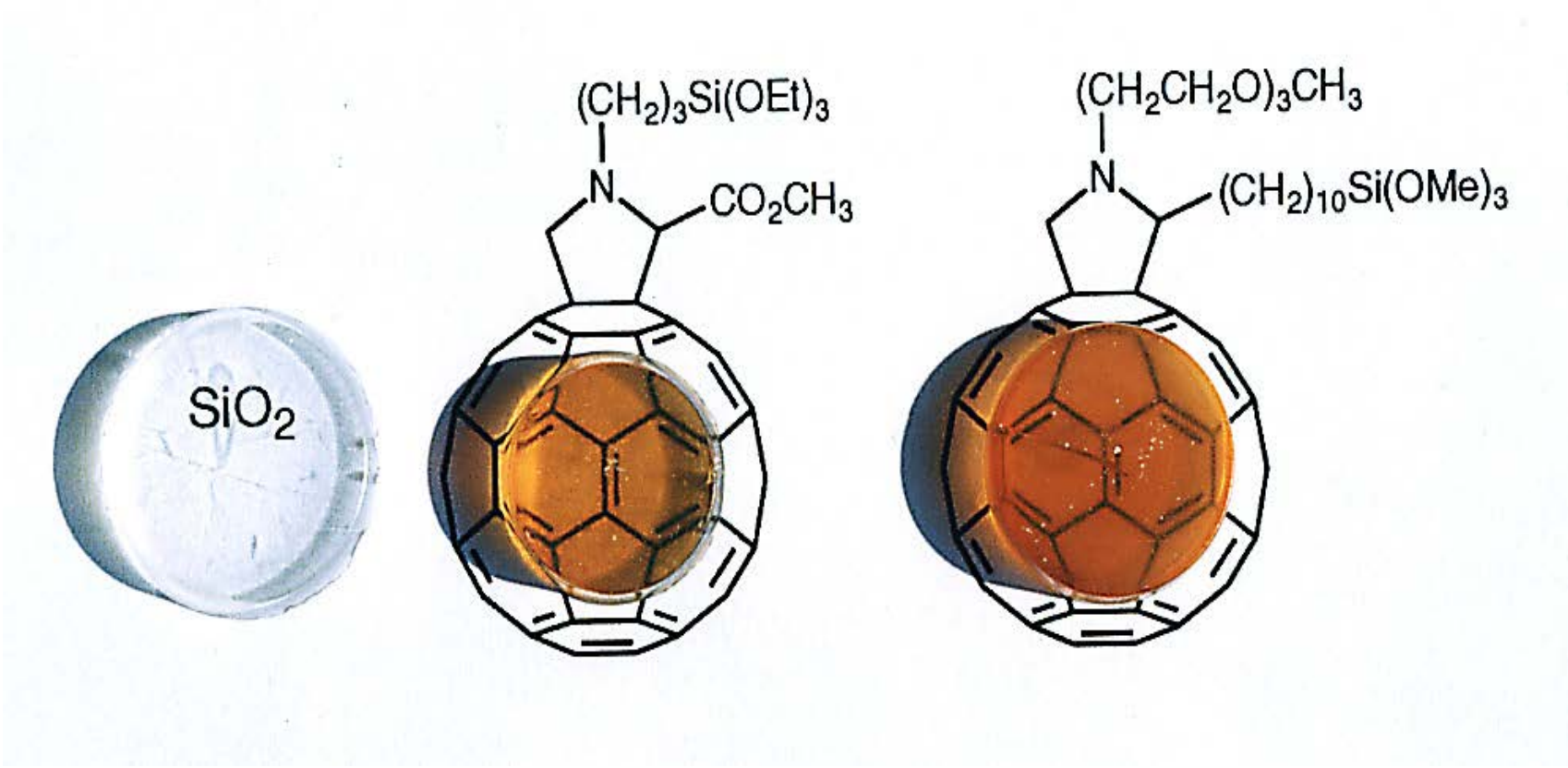


Coll. with M. Maggini

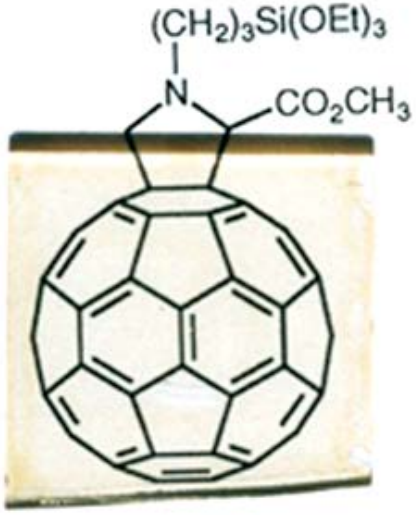
Solubility in tetrahydrofuran (mg/mL)

C_{60}	0
	1
	27
	43
	61
	216

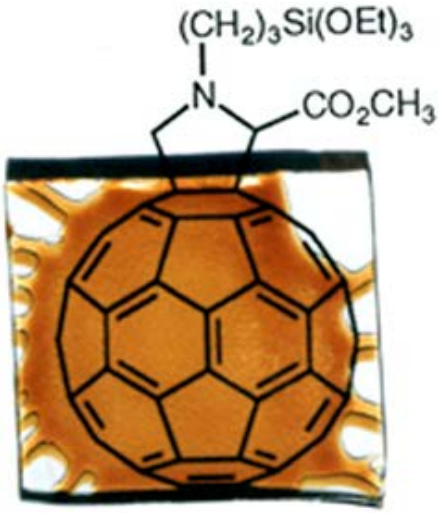
Functionalized C_{60} Sol-Gel Slabs



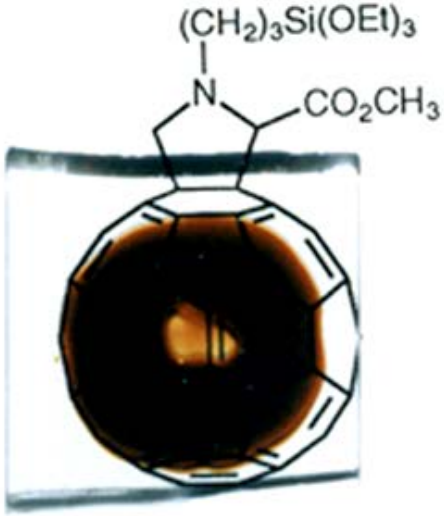
Chem. Eur. J. **1999**, 5, 2501-2510



6 μm
$(3 \cdot 10^{-3}M)$



30 μm
$(4 \cdot 10^{-3}M)$

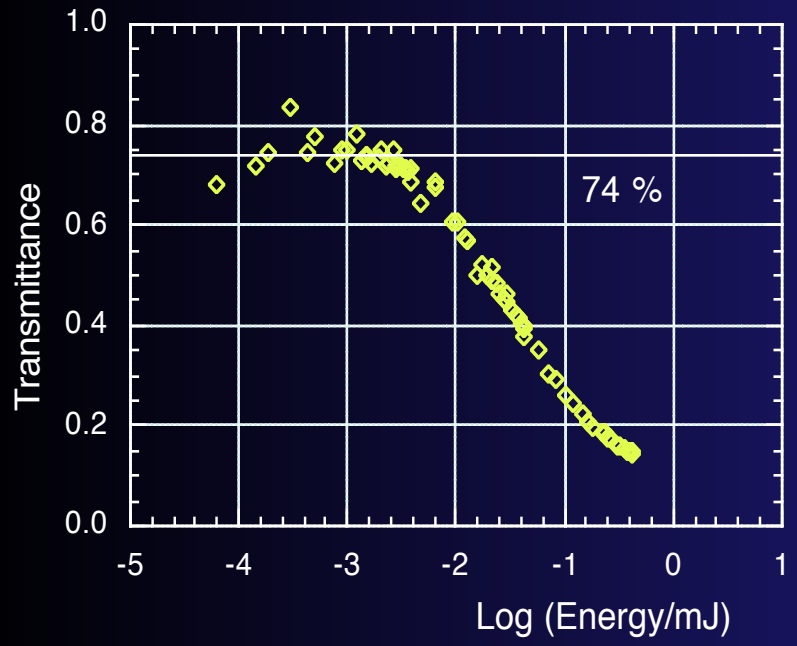


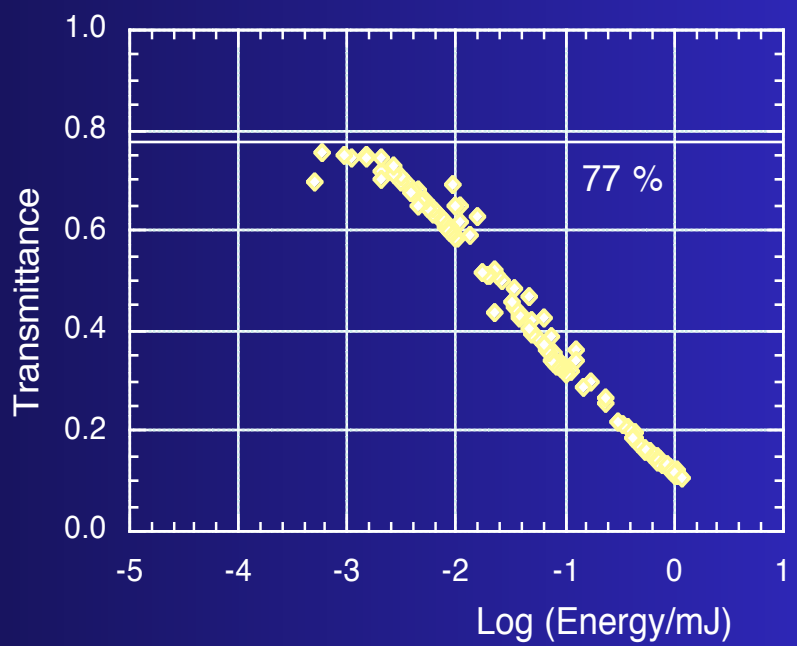
0.16 mm

coll. with G. Brusatin & M. Guglielmi

Toluene solution

Solid film





R. Signorini, M. Meneghetti, R. Bozio

Properties of Fulleropyrrolidines at 690 nm and of Sn-Phthalocyanine (Sn-Pc) at 532 nm

(one of the best RSA materials in the green)

FULP @ 690 nm

$\sigma_g = 1.1 \cdot 10^{-18}$ cm^2

$\sigma_e = 6.2 \cdot 10^{-17}$ cm^2

$\sigma_e - \sigma_g = 6.1 \cdot 10^{-17}$ cm^2

$\sigma_e / \sigma_g = 56$

$\Phi = 0.85 \div 0.90$

Sn-Pc @ 532 nm

$\sigma_g = 2.1 \cdot 10^{-18}$ cm^2

$\sigma_e = 6.7 \cdot 10^{-17}$ cm^2

$\sigma_e - \sigma_g = 6.5 \cdot 10^{-17}$ cm^2

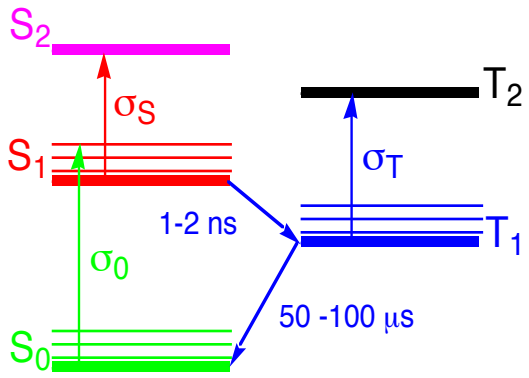
$\sigma_e / \sigma_g = 31$

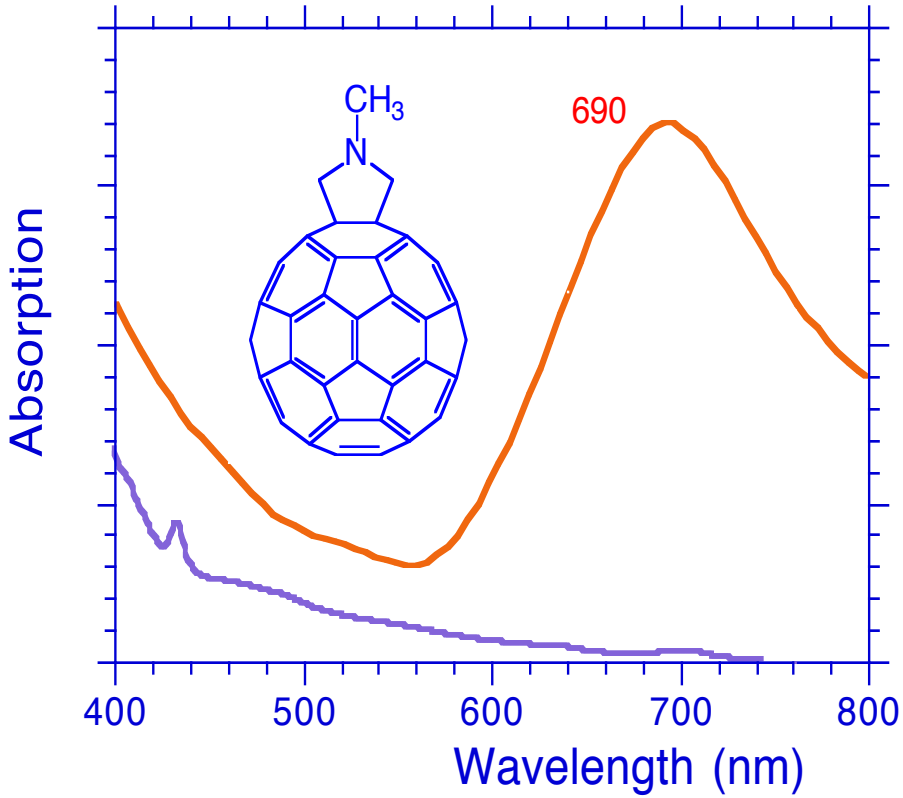
$\Phi = 0.55$

Ground State and First Triplet Excited State Absorptions in N-Methyl-Pyrrolidine

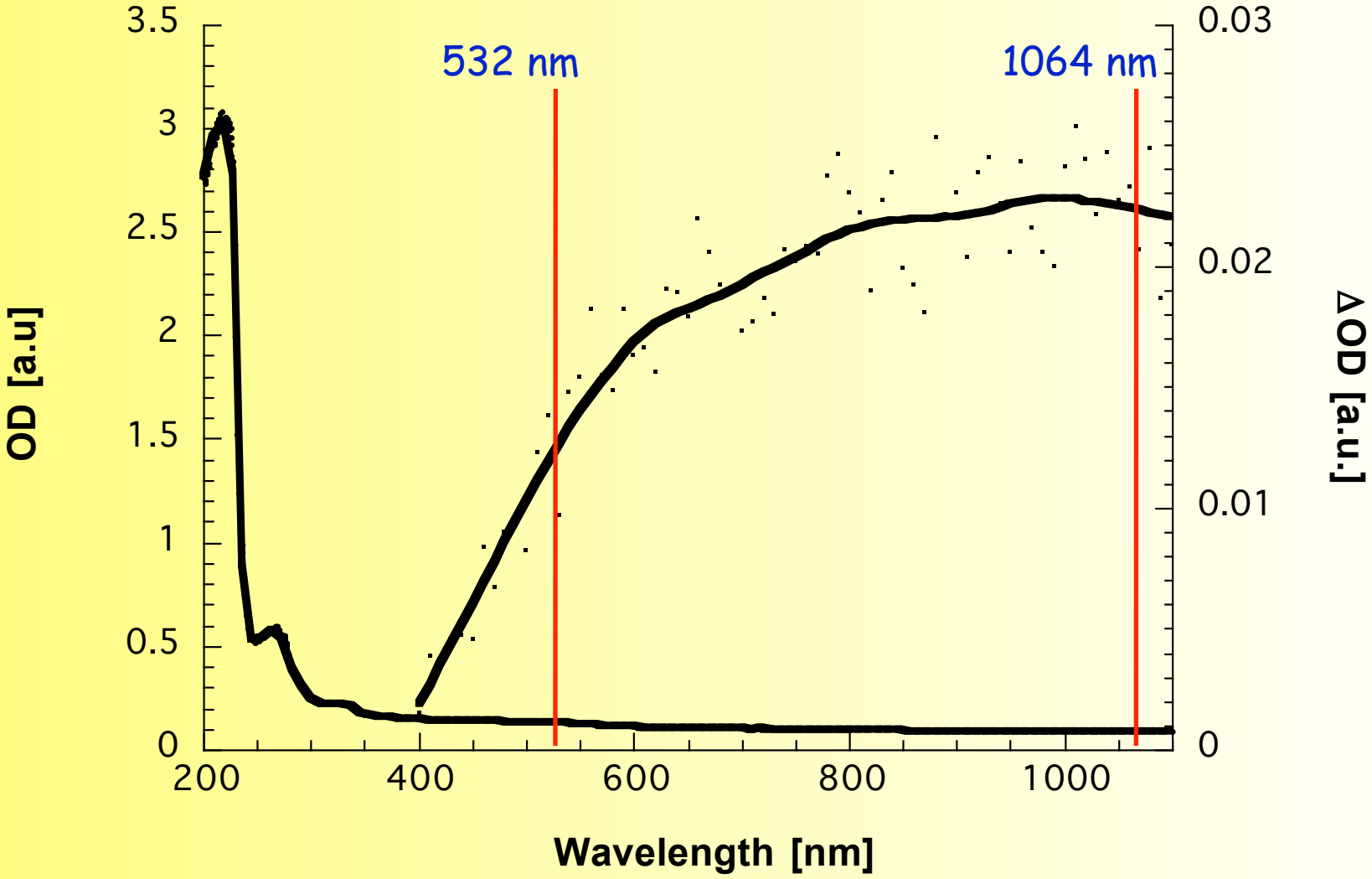
$$\Phi \geq 0.90$$

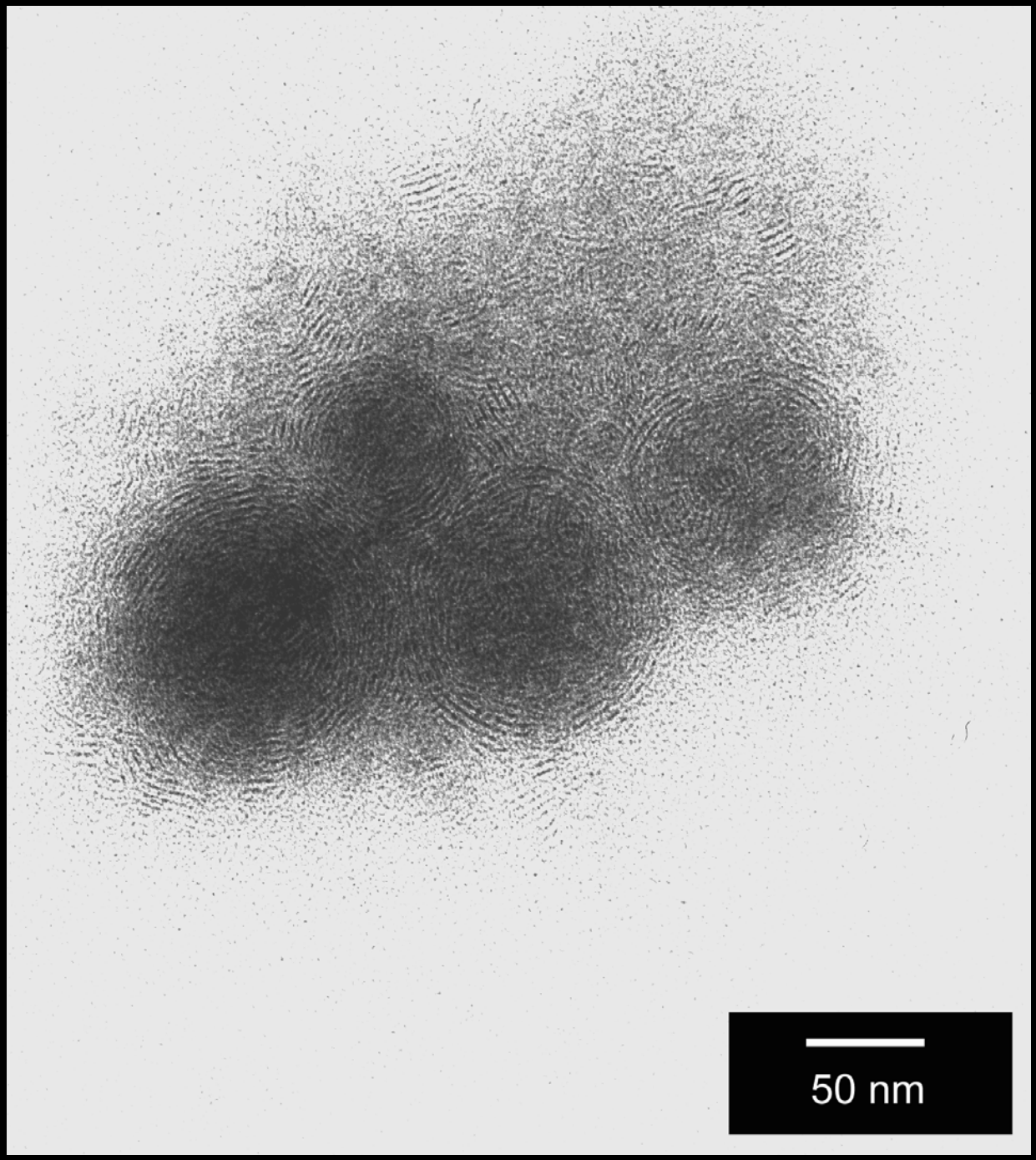
$$\frac{\sigma_T \propto (\varepsilon_T)}{\sigma_0 \propto (\varepsilon_0)} \gg 1$$

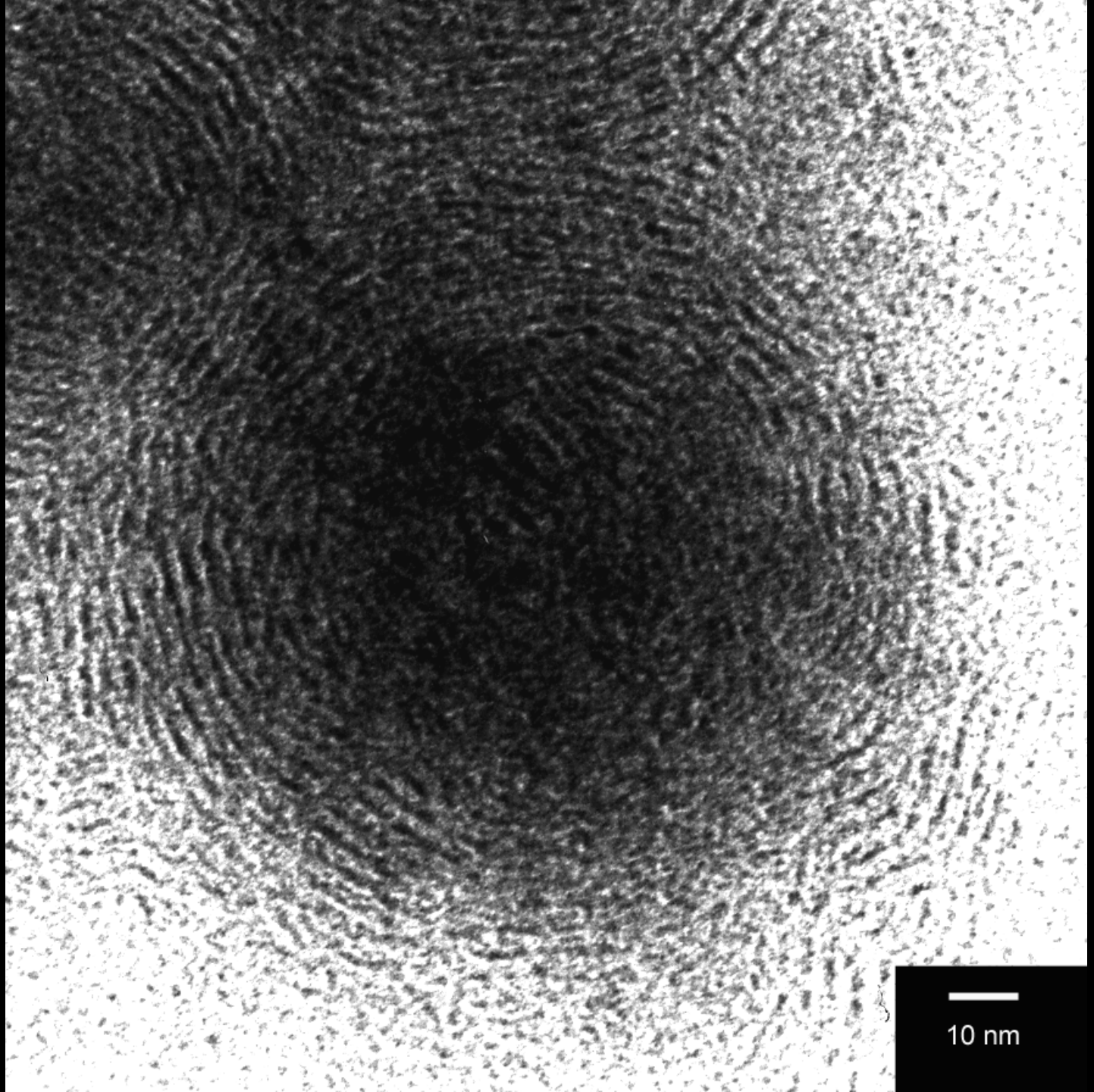




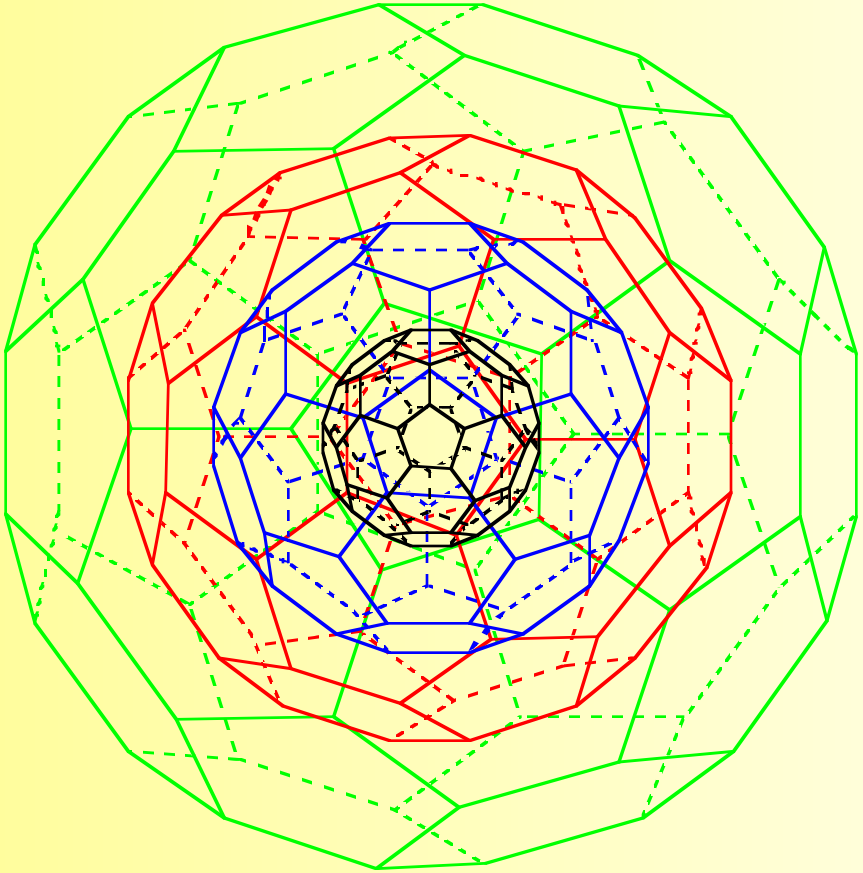
"Ideal" behavior of a broadband optical limiter



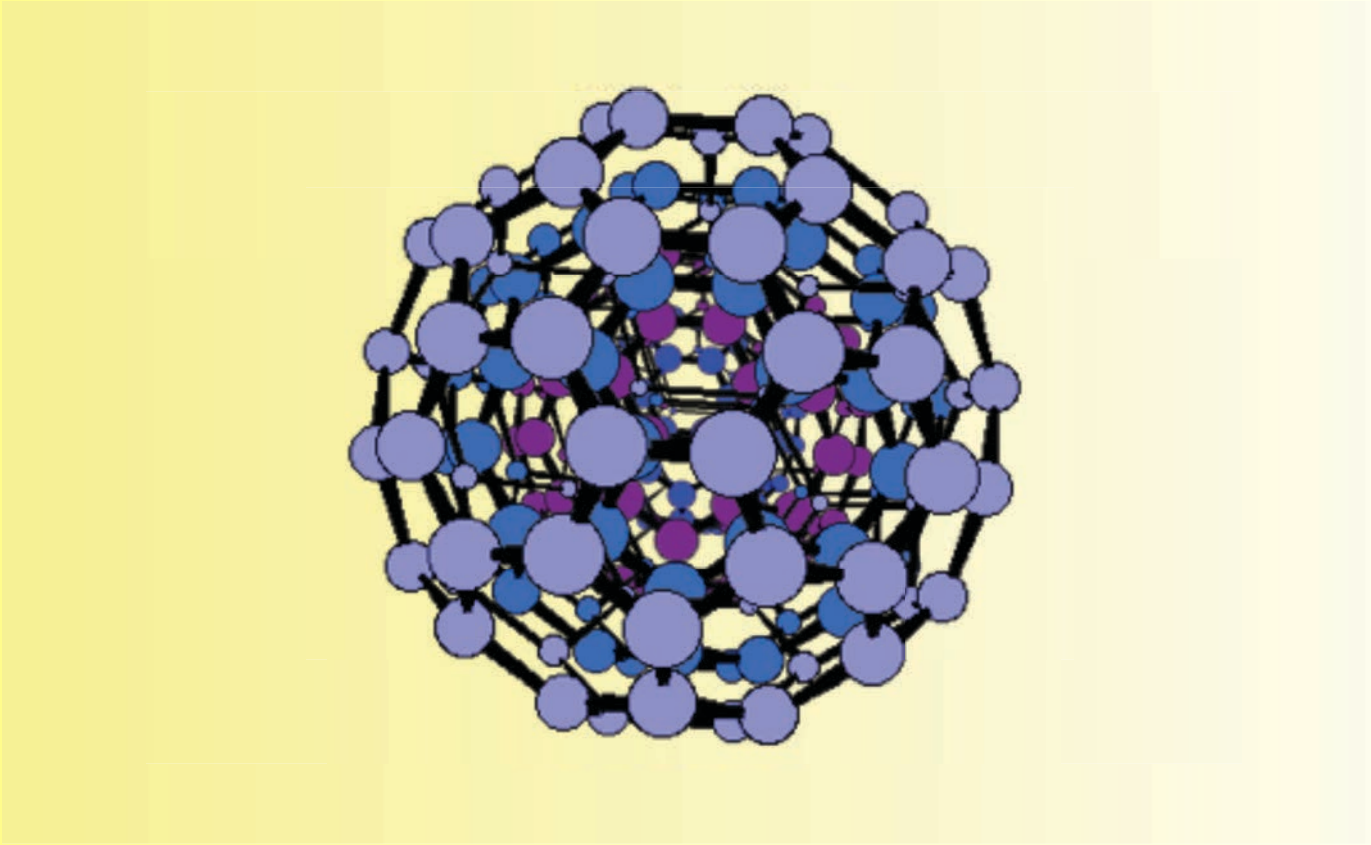

50 nm


10 nm

Carbon onions are made of concentric all-carbon cages



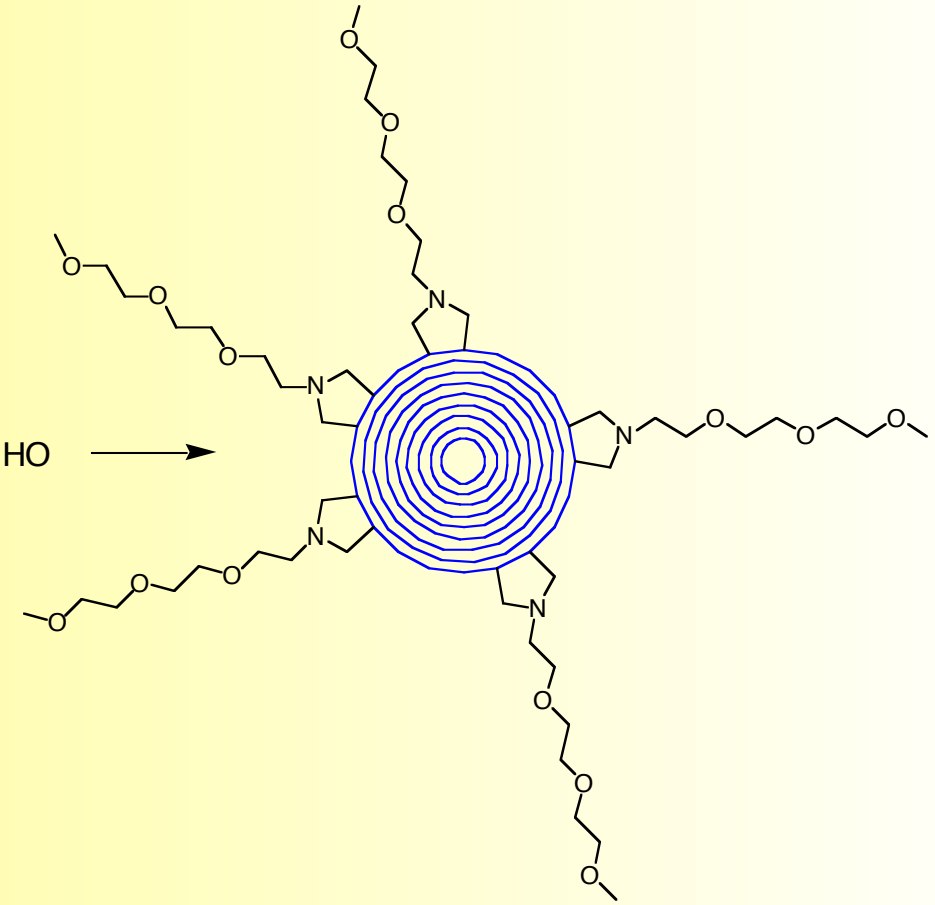
D. Ugarte, *Nature* **1992**, *359*, 707–709



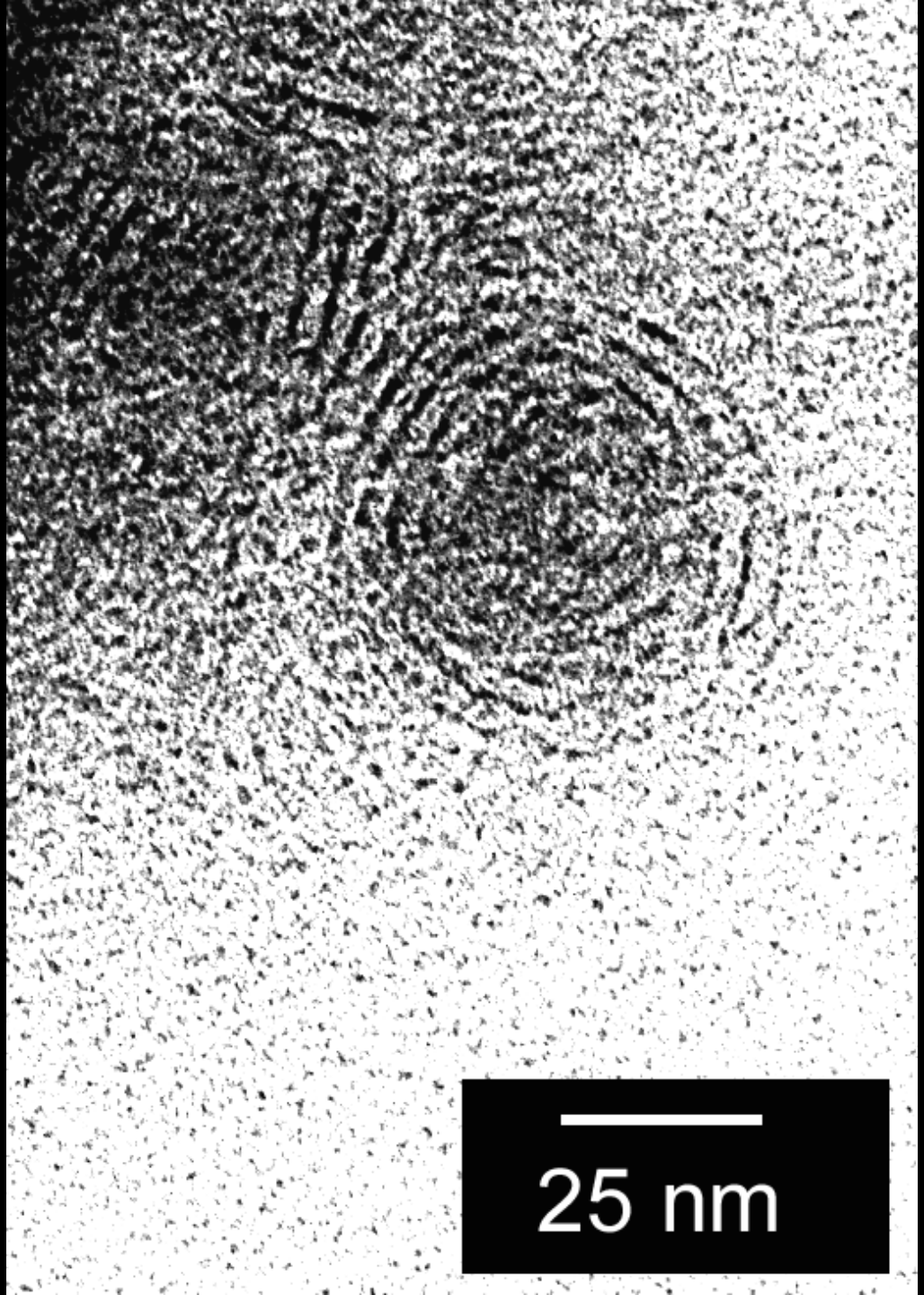
Carbon onions: S. Ijima 1980; D. Ugarte 1992

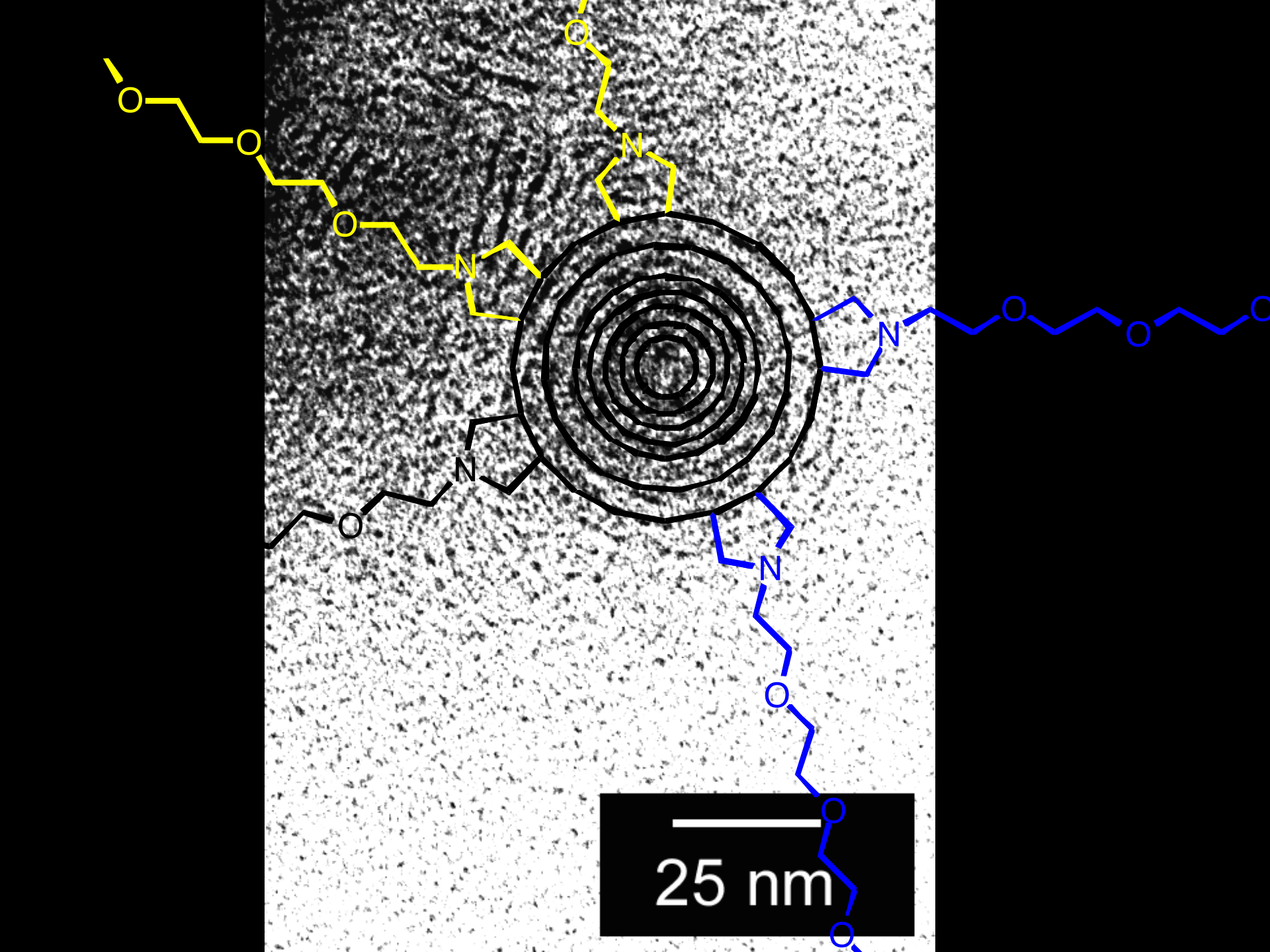
Organic functionalization of carbon onions

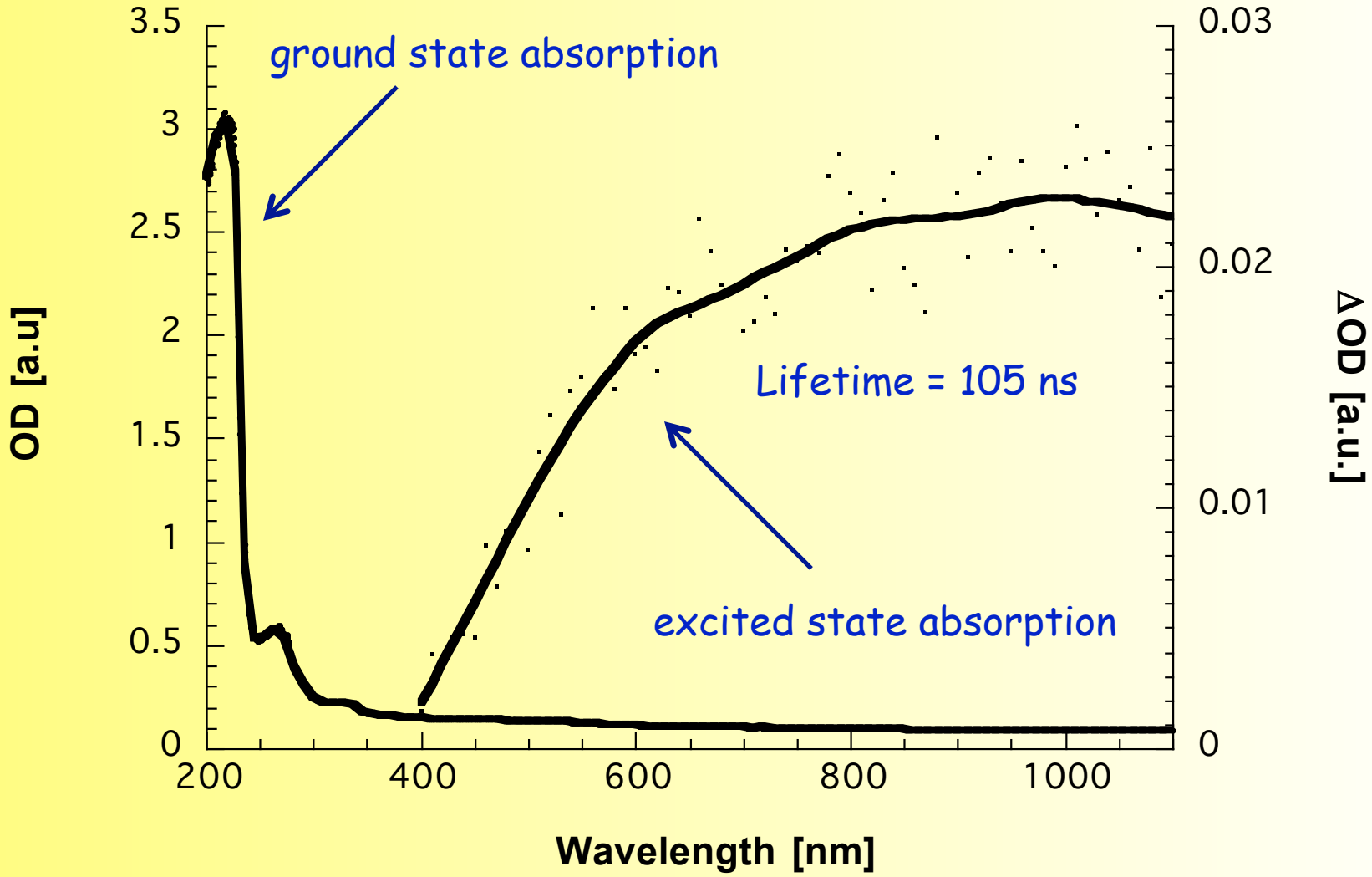
$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2NHCH_2COOH + HCHO \longrightarrow$

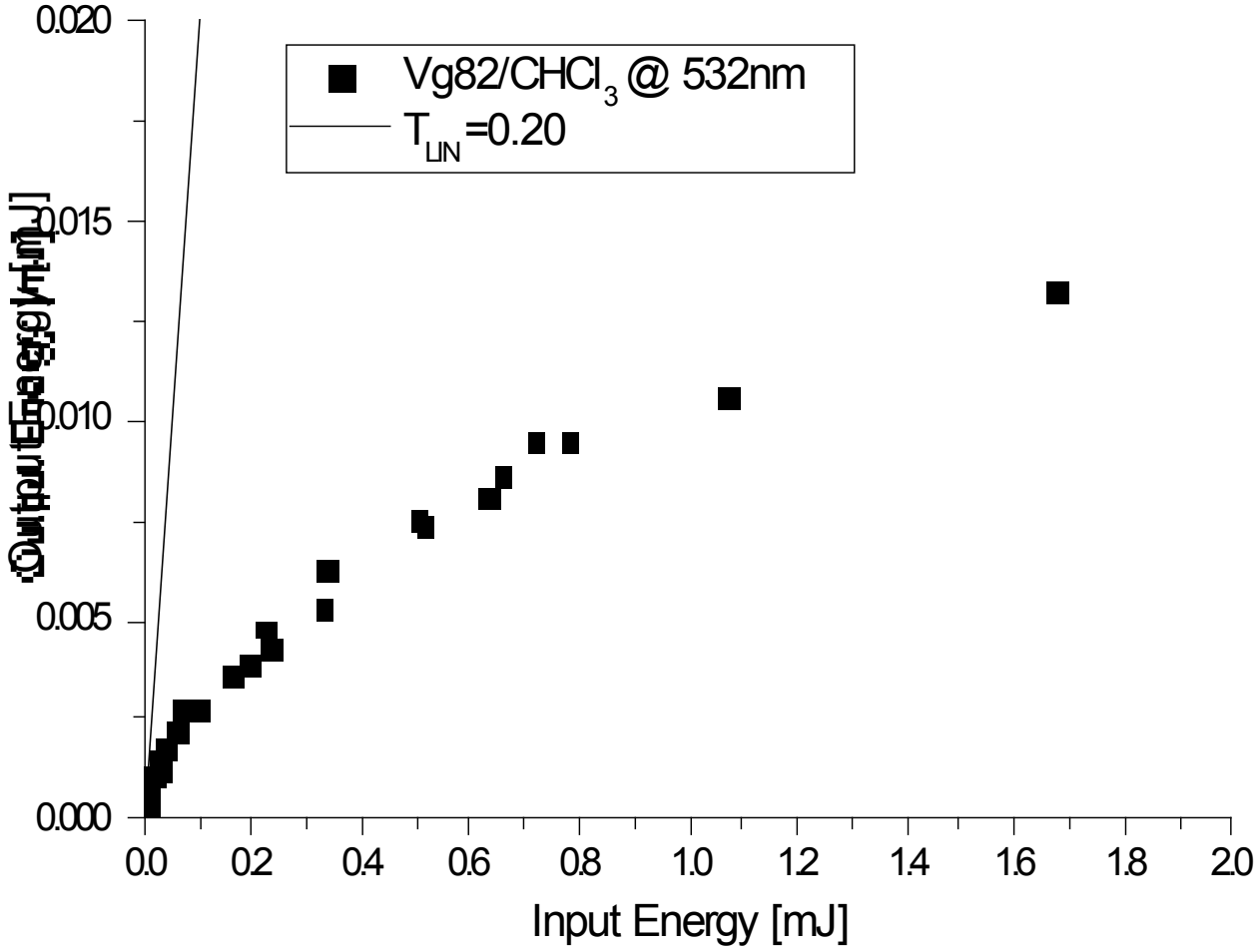


Soluble in chloroform (10 mg/ml)


25 nm


O
O
O
N
O
N
N
O
N
O
O
O
O
25 nm


ground state absorption
Lifetime = 105 ns
excited state absorption
OD [a.u]
ΔOD [a.u.]
Wavelength [nm]
3.5
3
2.5
2
1.5
1
0.5
0
0.03
0.02
0.01
0
200
400
600
800
1000


Vg82/CHCl3 @ 532nm
TLIN=0.20
0.020
0.015
0.010
0.005
0.000
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Input Energy [mJ]

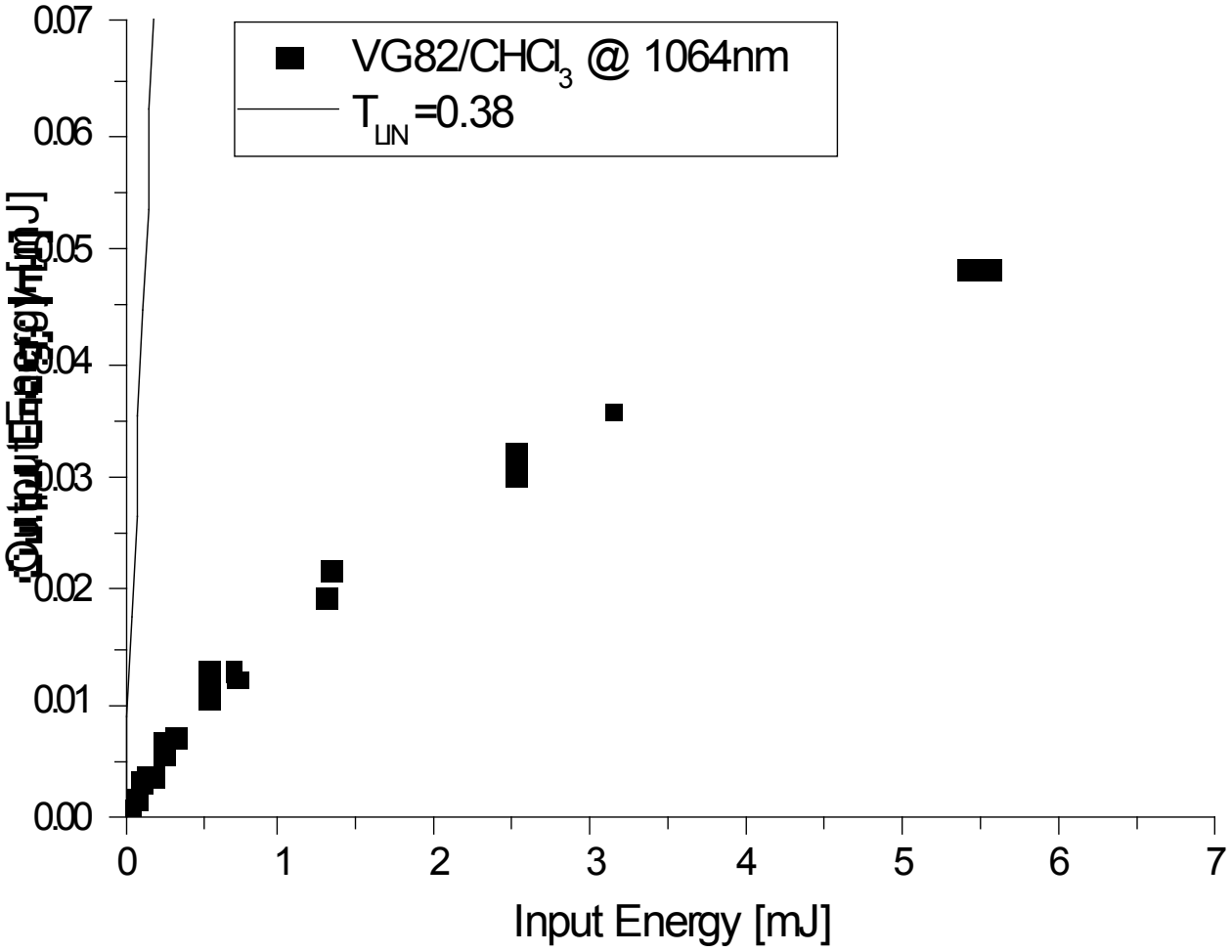

VG82/CHCl3 @ 1064nm
TLIN=0.38
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
0
1
2
3
4
5
6
7
Input Energy [mJ]

Figure of Merit = T_{lin}/T_{NL}

FOM = 20 @ 532 nm

FOM = 40 @ 1064 nm

First example of a material in solution, working as optical limiter in a broad visible-NIR range, showing increasingly good performances as one enters the IR region