

Materials design & selection for Circular Economy

Module 3: Molecules and materials chemico-physical characterisation

Academic year 2026/2027

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Molecular luminescence

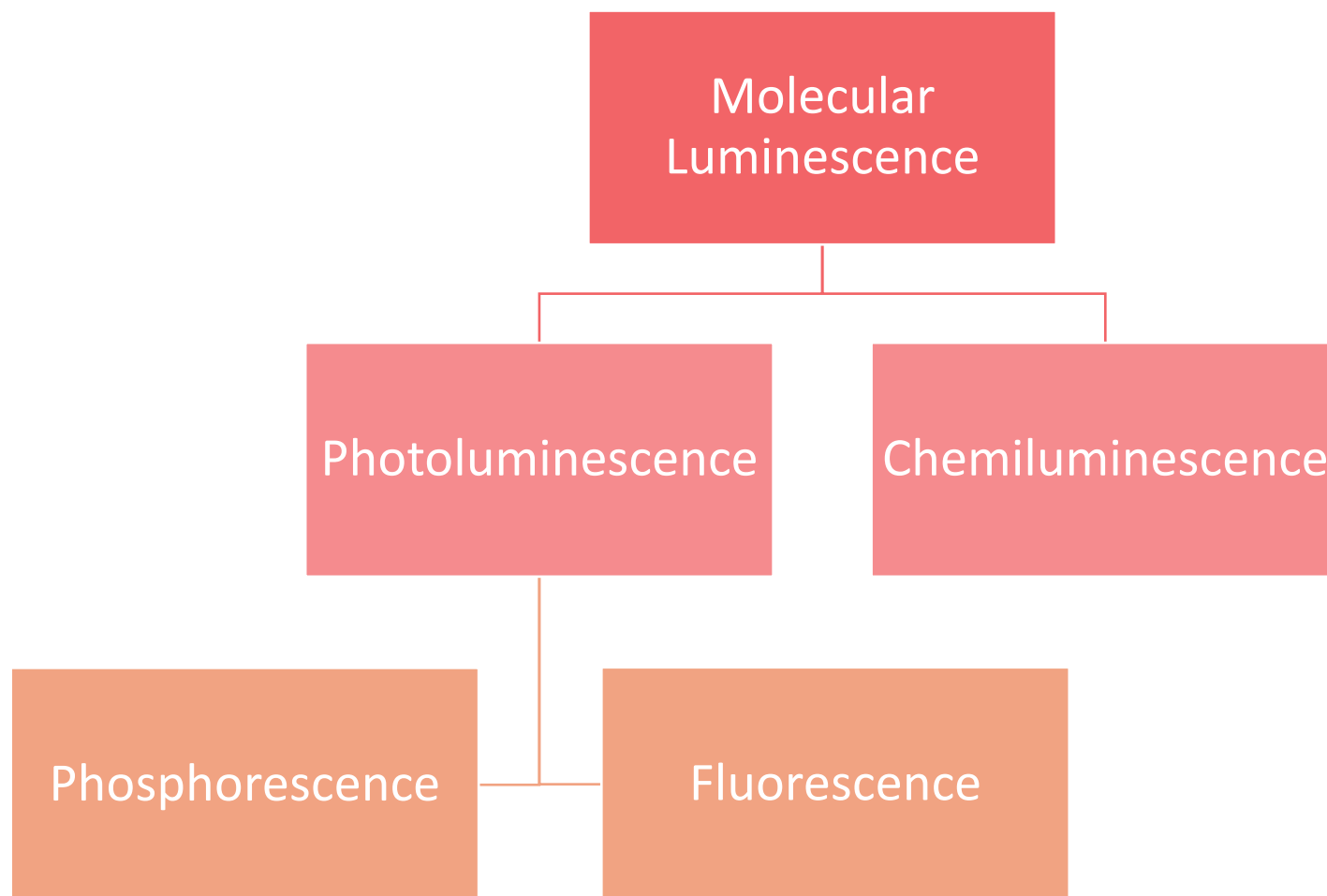


Photo- vs chemiluminescence



Photoluminescence

- Exploits photons to reach the excited state
- Concurring effects might lower S/N ratio
- Non-destructive & repeatable

Chemiluminescence

- Exploits a chemical reaction to reach the excited state
- Higher detection sensitivity
- Single-use: stops when chemical precursors are consumed

Bioluminescence



https://www.youtube.com/watch?v=fjQmTNUpa_s

Luminescence

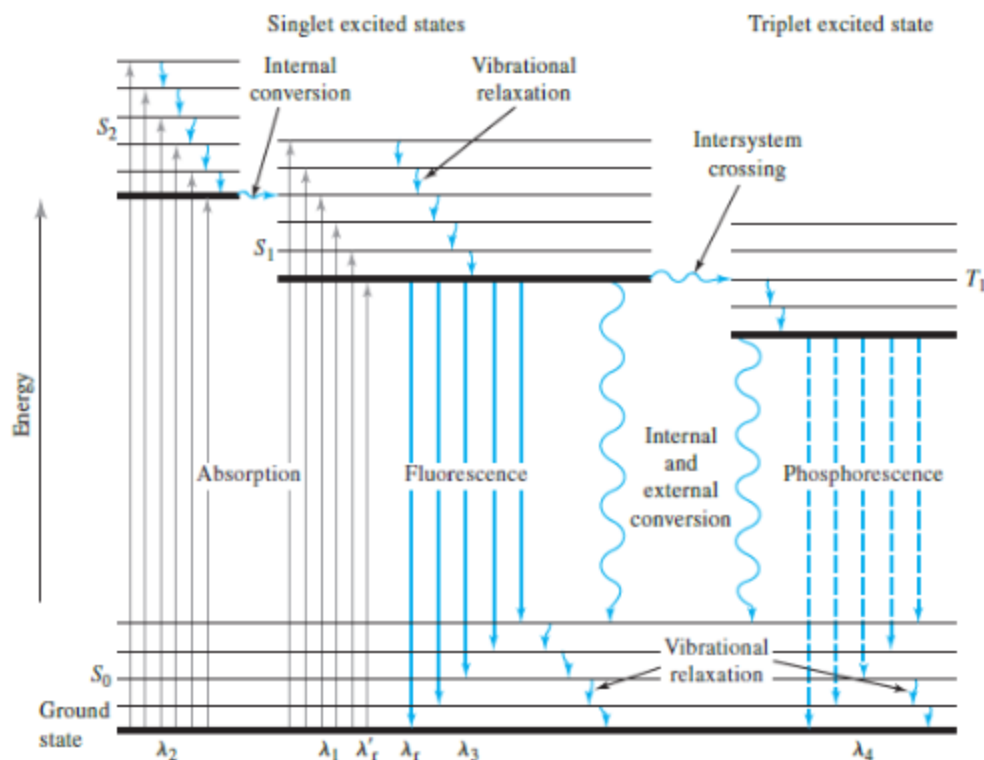


FIGURE 15-2 Partial energy-level diagram for a photoluminescent system, often called a Jablonski diagram.

Jablonski diagram

- **Absorption** lasts 10^{-14} - 10^{-15} s.
- **Fluorescence** lasts 10^{-5} - 10^{-10} s.
- **Phosphorescence** lasts 10^{-4} - 10 s.
- **Deactivation processes** of the **excited state** can either emit photon such as fluorescence and phosphorescence (*radiative deactivation*) or be radiationless.
- Excited-state deactivation favors the fastest available relaxation pathway.
- Since the vibrational relaxations are faster than the lifetime of an excited electronic state, fluorescence occurs always from the lowest excited vibrational state to the ground state. This leads to **Stokes shift** ($\lambda_{\text{fluor}} < \lambda_{\text{exc}}$).

Electron spin



- Electronic spin states of molecules play a crucial role in determining the deactivation process
- Ground state, electrons are paired: diamagnetic state
- Diamagnetic state in a magnetic field show no further splitting → **Singlet** state
- Unpaired electrons: paramagnetic state
- Paramagnetic state can adopt two states in a magnetic field → **Triplet** state
- Excitation to a triple state less probable but possible

Pauli exclusion principle: **no 2 electrons** in the same molecular orbital with the **same spin state**

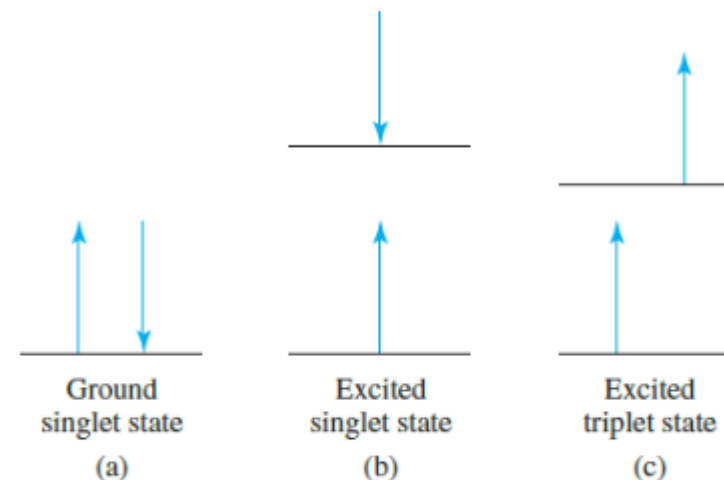


FIGURE 15-1 Electronic spin states of molecules. In (a) the ground electronic state is shown. In the lowest energy, or ground, state, the spins are always paired, and the state is said to be a singlet state. In (b) and (c), excited electronic states are shown. If the spins remain paired in the excited state, the molecule is in an excited singlet state (b). If the spins become unpaired, the molecule is in an excited triplet state (c).

Deactivation processes

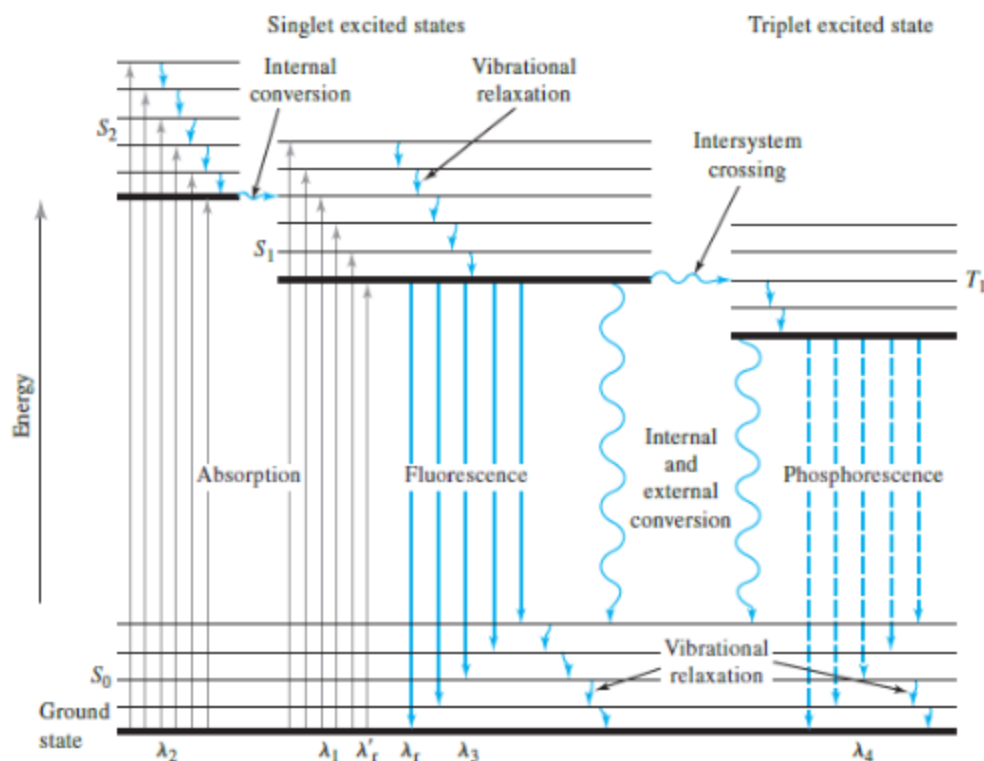


FIGURE 15-2 Partial energy-level diagram for a photoluminescent system, often called a Jablonski diagram.

Jablonski diagram

- **Internal conversion:** overlap of vibrational states of different excited electronic states. Same multiplicity is necessary ($S \rightarrow S$; $T \rightarrow T$). Extremely efficient process
- **External conversion:** radiationless process, excess energy is transferred to solvent molecules. Lowering T and using viscous solvent can decrease it
- **Fluorescence:** decay from an excited electronic state to the ground state
- **Intersystem crossing:** crossover between electronic states of different multiplicity. ISC is necessary to have phosphorescence. Presence of heavy atoms (e.g., I) or paramagnetic species (e.g., O_2 , Cu^{2+}) in the system increases ISC probability (spin-orbit coupling)
- **Phosphorescence:** decay from a triplet excited state to a singlet ground state. Spin-forbidden transition, very slow. Presence of heavy atoms also improves phosphorescence, but paramagnetic species favor non-radiative $T \rightarrow S$ relaxations, quenching phosphorescence

Internal conversion might lead to transfer of e- to anti-bonding molecular orbitals $\rightarrow$ bond weakening

Quantum yield



- The quantum yield ϕ is a measure of effectively the absorbed photons are converted into luminescence

$$\phi = \frac{k_f}{k_f + k_i + k_{ec} + k_{ic} + k_{pd} + k_d}$$

k_f : fluorescence rate constant

k_i : ISC rate constant

k_{ec} : external conversion rate constant

k_{ic} : internal rate constant

k_{pd} : predissociation rate constant

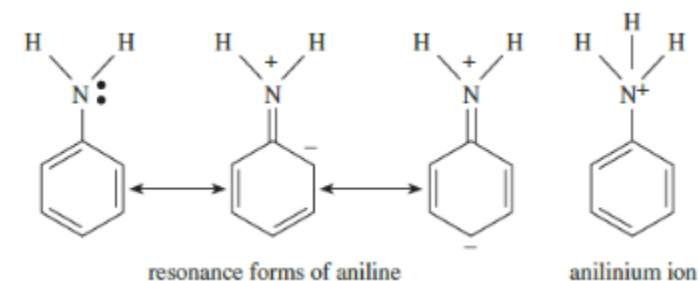
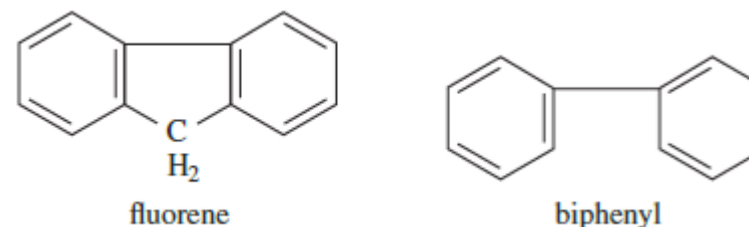
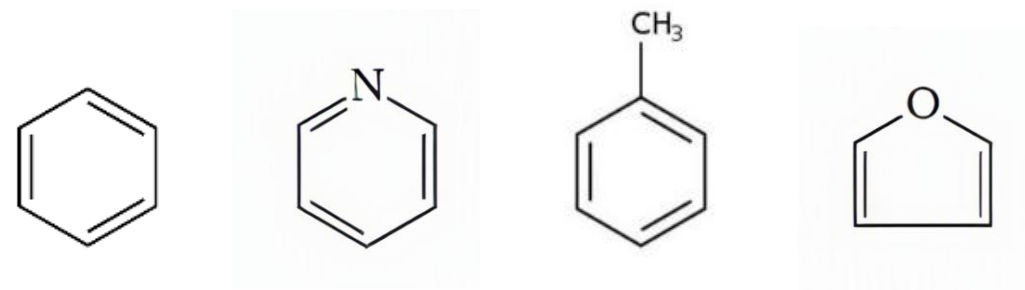
k_d : dissociation rate constant

 depend on the chemical backbone of the molecule
 depend on the surrounding environment

Factors affecting quantum yield



- **Aromaticity** induces fluorescence, but heterocyclic compounds do not.
- **Structural rigidity** confers improved quantum yields.
- **Temperature** increases the number of collisions, namely it improves external conversion. The solvent viscosity decreases by increasing the temperature.
- **Solvent** containing heavy atoms (carbon tetrabromine, ethyl iodide) induces triplet states.
- **Changes of pH** can affect the resonant forms of pH-dependent species like aniline
- **Concentration** of the luminescent analyte affects the fluorescent emission

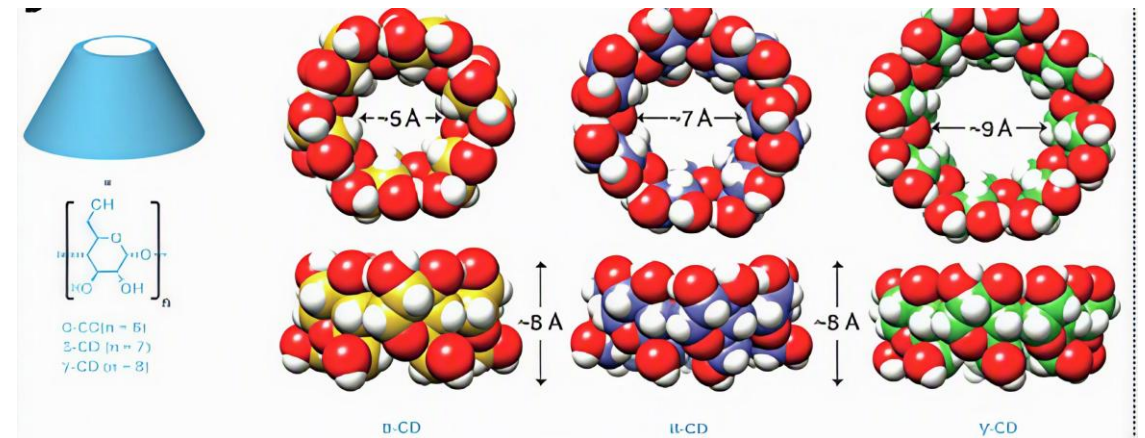


The diagram illustrates the quenching and enhancing mechanism of P-CNDs by metal ions. It shows a central state of P-CNDs free (λ_{em} 560 nm, QY ~ 12%) which can be quenched by Mn²⁺, Hg²⁺, Fe³⁺, Fe²⁺, Cu²⁺, Sn⁴⁺, Sn²⁺, Ni²⁺, and Co³⁺, resulting in 'No PL'. Alternatively, it can be enhanced by Al³⁺, Zn²⁺, and Cd²⁺ to form P-CND:Al³⁺ (λ_{em} 495 nm, QY ~ 61%), P-CND:Zn²⁺ (λ_{em} 525 nm, QY ~ 40%), and P-CND:Cd²⁺ (λ_{em} 530 nm, QY ~ 30%) respectively. The process is labeled 'Quenching' and 'Enhancing' with arrows.

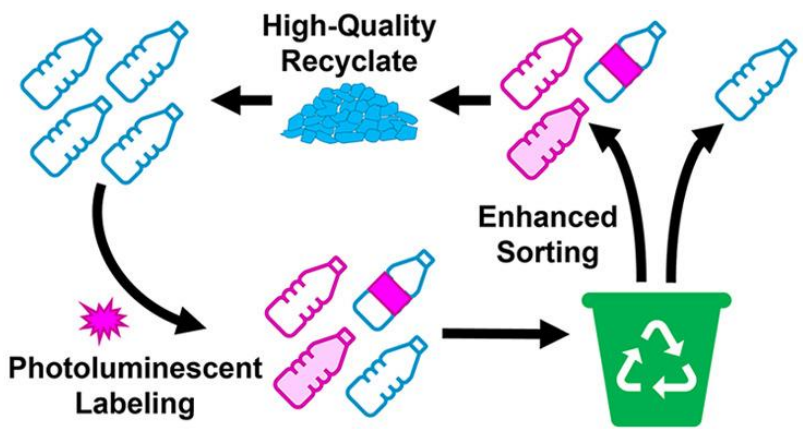
Phosphorimetric methods



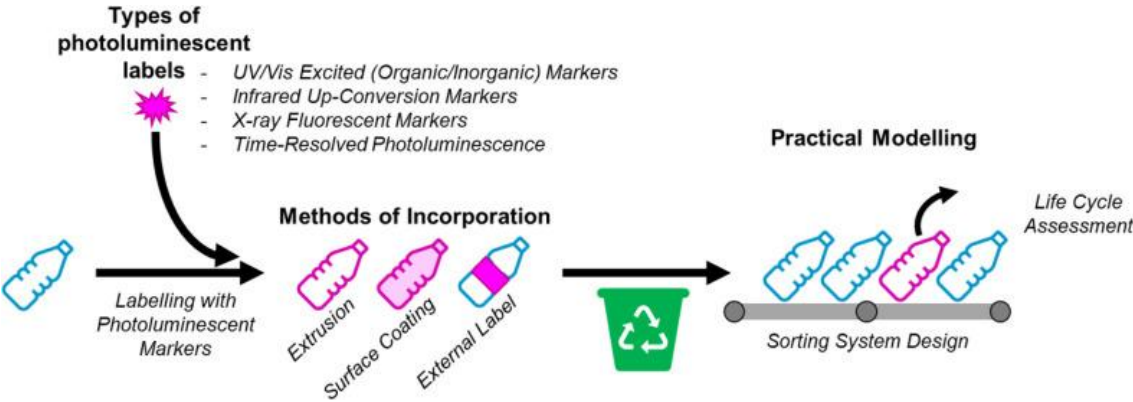
- These methods are less common than fluorimetric assays:
 - Temperature sensitivity: analysis should be performed under cryogenic conditions
 - Less precision: due to frozen samples, cracks and inhomogeneity affect reproducibility
- Phosphorescence is more selective than fluorescence:
 - Due to the longer lifetime, it is possible to introduce a measuring delay $\rightarrow$ improvement of S/N ratio
- Solution: immobilize the analyte on a solid support (silica gel, membranes) $\rightarrow$ minimized collisional quenching



Enabling the Polymer Circular Economy

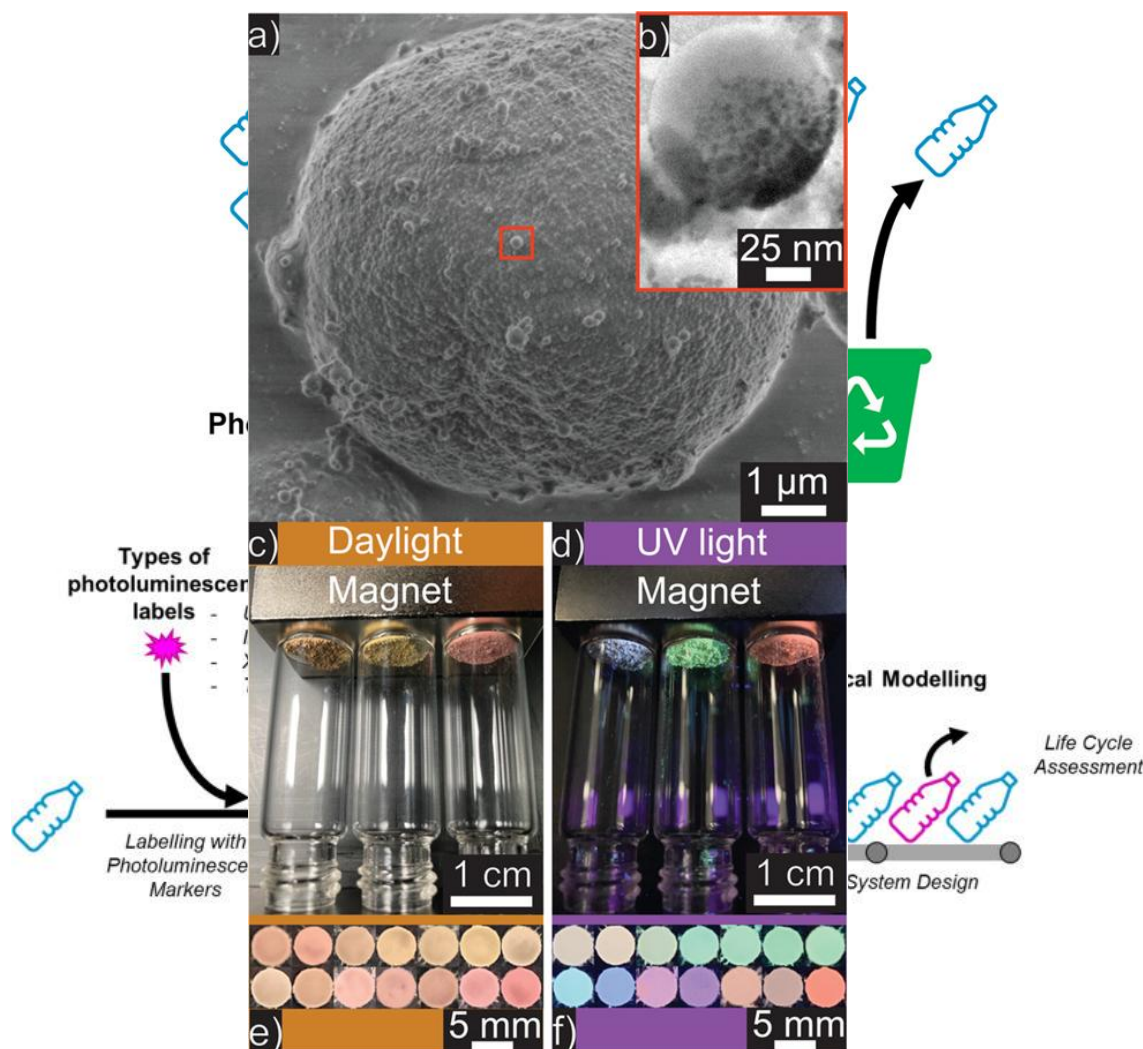


- Typical plastic wastes are sorted by:
 - Manual sorting
 - Sink-float or froth flotation
 - Infrared or optical color recognition



	organic	inorganic
	e.g. perylenes, coumarins, rhodamines, and quinolines.	e.g. metal complexes and rare earth metal oxides.
photoluminescent quantum yield	variable, but generally high; highly dependent upon the solvent/environment	variable, but generally quite low
molar absorbance	variable, but generally high	variable, depending on ligand structure
emission spectra	broad, around 40–70 nm half-width	narrow, around 10 nm half-width
Stokes shift	variable, commonly around 10–100 nm	quite large, around 100–200 nm
photoluminescent lifetime	short, around 0.5–5 ns	long, can be up to 1 ms
photostability	variable, but generally poor	relatively high
toxicity	variable, but often low	less definitive data available, can be quite high

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<https://doi.org/10.1021/acspolymersau.2c00040>