Unraveling the Optical Signatures of Polymeric Carbon Nitrides: Insights into Stacking-Induced Excitonic Transitions

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Supporting Information Available

Experimental and computational methods

Computational details

Calculations were conducted using the Vienna Ab initio Simulation Package (VASP) version 6.3.2, which utilizes the projector-augmented wave (PAW) method.¹⁻⁵ A plane wave energy cut-off of 400 eV was employed, and the wavefunction was optimized to an accuracy of 10^{-6} eV. Atomic coordinates were relaxed until the forces reached below 5×10^{-2} eV/Å. Gaussiantype finite-temperature smearing with a width of 0.01 eV was applied. DFT-D3 dispersion correction was utilized to account for long-range interactions.^{6,7} The atomic and cell coordinates were relaxed using the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional within the generalized gradient approximation (GGA).⁸ Accurate final energy results were obtained by performing single-point calculations on the PBE-optimized structures using the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional, which includes 25% exact exchange and a screening factor of 0.2 \AA^{-1} .⁹ The HSE06 functional was found to provide a good description of the electronic properties of PCNs. For the monolayer, a vacuum layer with a thickness of 20 Å was added to avoid interactions between the periodic images, and dipole correction was applied. The Brillouin zone integration for periodic models was performed using Gamma-centered k grids. The excitonic effects were calculated including the frequencydependent dielectric functions and the oscillator strength by the time-dependent Hartree-Fock (TDHF) implanted in VASP.^{10,11} The details are described in the Supporting Information and all data used in this study is available via Zenodo.¹²(DOI:10.5281/zenodo.10844460)

Sample preparation and diffuse reflectance spectroscopy

The conventional yellow coloured polymeric carbon nitride was prepared by thermal polycondensation of 30 g melamine at 530 °C for 4 h in a lid-covered crucible. Diffuse reflectance UV-vis spectra of solid was recorded using a Shimadzu UV2600 UV-vis spectrophotometer.

Supplementary methods

The optical excitation energy is obtained from the transition matrix within the adiabatic linear response theory:¹³

$$\begin{bmatrix} A & B \\ -B^* & -A^* \end{bmatrix} \begin{bmatrix} \mathbf{X}_s \\ \mathbf{Y}_s \end{bmatrix} = E_s \begin{bmatrix} \mathbf{X}_s \\ \mathbf{Y}_s \end{bmatrix}$$
(1)

where E_s is the excitation eigenvalues, X_s and Y_s are corresponding wavefunctions, A and $-A^*$ are the resonant transition and antiresonant transitions from occupied orbitals to unoccupied orbitals, and B and $-B^*$ are the coupling between the excitations and de-excitations, respectively. In the HSE@Casida formulation, the matrices A: $A_{vc}^{v'c'} = (\varepsilon_v^{\text{HSE}} - \varepsilon_c^{\text{HSE}}v)\delta_{vv'}\delta_{cc'} + \langle cv'|V|vc'\rangle - \langle cv'|f_{xc}|c'v\rangle$, and the matrices B: $B_{vc}^{v'c'} = \langle vv'|V|cc'\rangle - \langle vv'|f_{xc}|c'c\rangle$, where the occupied v, v' and unoccupied c, c' states, include that interactions between electrons and holes are described by an effective nonlocal frequency-dependent kernel f_{xc} .¹⁴ The Tamm-Dancoff approximation (TDA) neglects the off-diagonal coupling elements. Hence, the Eq. (1) reduces to $AX_s = E_s X_s$.¹⁵ The macroscopic dielectric matrix $\epsilon_M(\mathbf{q}, \omega)$ is obtained by an inversion of the full microscopic dielectric matrix in giving long-wavelength limit $\mathbf{q} \to 0$. It gives $\epsilon_M(\mathbf{q}, \omega) = (\epsilon_{0,0}^{-1}(\mathbf{q}, \omega))^{-1}$. Exploiting the TDA approximation, the solution of HSE@Casida $(E_s \text{ and } X_s)$ can be used to obtain the macroscopic dielectric function:

$$\epsilon_{\rm M}^{\alpha\alpha}(\mathbf{q},\omega) = 1 + \frac{2}{\Omega} \frac{e^2 \hbar^2}{\epsilon_0 m_0^2} \sum_s \left(\left| \sum_{c,v,\mathbf{k},m} \frac{\langle c\mathbf{k}m | p_\alpha | v\mathbf{k}m \rangle}{\epsilon_{c\mathbf{k}}^m - \epsilon_{v\mathbf{k}}^m} ^* X_s^{c,v,\mathbf{k}} \right|^2 \times \sum_{\beta=\pm 1} \frac{1}{E_s - \beta \hbar(\omega + i\eta)} \right), \quad (2)$$

where p is the momentum operator with Cartesian coordinates α , m is z-component quantum number, Ω is the lattice volume, and η is an infinitesimal number related to the exciton lifetime.^{16,17} The oscillator strength f^s_{α} of state s is given by

$$f_{\alpha}^{s} \propto E_{s} \left| \sum_{c,v,\mathbf{k},m} \frac{\langle c\mathbf{k}m | p_{\alpha} | v\mathbf{k}m \rangle}{\epsilon_{c\mathbf{k}}^{m} - \epsilon_{v\mathbf{k}}^{m}} X_{s}^{c,v,\mathbf{k}} \right|^{2}.$$

$$(3)$$

The imaginary part of the dielectric function for 3×3 Cartesian tensor is given by

$$\epsilon_{\rm M}^{2,\alpha\alpha}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \to 0} \frac{1}{q^2} \sum_{c,v,\mathbf{k},m} 2w_{\mathbf{k}} \delta(\varepsilon_{c\mathbf{k}+\mathbf{q}} - \varepsilon_{v\mathbf{k}} - \omega) \times \langle u_{c\mathbf{k}+q\mathbf{e}_{\alpha}} | u_{v\mathbf{k}} \rangle \langle u_{v\mathbf{k}} | u_{c\mathbf{k}+q\mathbf{e}_{\alpha}} \rangle.$$
(4)

, where the \mathbf{e}_{α} is unit vectors for cartesian coordinates, $w_{\mathbf{k}}$ is k-point weights, and u is the Bloch vector, respectively. The real part of the dielectric tensor $\epsilon_{\mathbf{M}}^{\mathrm{real},\alpha\alpha}(\omega)$ is obtained by Kramers–Kronig relations

$$\epsilon_{\rm M}^{\rm real,\alpha\alpha}(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\epsilon_M^{\rm img,\alpha\alpha}(\omega')\omega'}{\omega'^2 - \omega^2} \, d\omega \,. \tag{5}$$

From the real and the imaginary parts of dielectric functions, the absorption coefficient is calculated. 18

Supplementary data



Figure S1: The band structure (left) and its orbital projection (right) of (a) melon-2D, (b) PHI-2D, (c) pg–CN-2D, and (d) cg–CN-2D. The projection is performed on s, p orbitals corresponding to carbon and nitrogen atoms. The trivial contribution of hydrogen is omitted. Fermi energy is referenced to 0 eV.

Structure	bandgap (eV)	Structure	bandgap (eV)
melon-2D	3.68	melon-3D	3.12
PHI-2D	3.32	PHI-3D	3.18
cg-2D	2.99	cg-3D	2.95
pg-2D	2.79	pg-3D	2.35

Table S1: The calculated bandgap (HSE06) of PCN structures.



Figure S2: The depiction of electron density in (a) melon, (b) PHI, (c) cg, and (d) pg 2D structures corresponding to the respective energy level at Γ .



Figure S3: The calculated imaginary part of the dielectric function for pg-2D structure using TD@Casida (black), GW@BSE (red)¹⁹, and $GW@IP^{19}$ (blue) calculations. The scissor correction is applied based on the brightest state, which is commonly located around 4 eV.

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