Supporting Information: Excitons and Solar-Harvesting Potential of γ-Graphyne

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S1 Computational Details

To investigate these properties in γ-graphyne, DFT simulations were conducted utilizing the Vienna Ab Initio Simulation Package (VASP)[S1] with the Projector Augmented-Wave (PAW)[S2] method. We did geometry optimizations using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional[S3]. A plane-wave cutoff energy of 550 eV was used, and a Monkhorst–Pack k-point mesh of $10 \times 10 \times 1$ was used to sample the Brillouin zone for geometry optimizations and $20 \times 20 \times 1$ for electronic band structure and density of states calculations. A vacuum spacing of 20 Å was used in the out-of-plane direction to prevent spurious interactions between periodic images. We achieved structural convergence using thresholds of 10^{-6} eV for the total energy and 0.01 eV Å^{-1} for the residual forces.

Although the precise structural parameters may exhibit small quantitative variations depending on the exchange–correlation functional, the overall planar topology of pristine γ-graphyne is robust. Since the system is treated here as a periodic monolayer, supercell-size effects are not expected to qualitatively alter the optimized primitive-cell geometry. In this context, the most relevant finite-size parameter is the vacuum separation.Case report

To address the well-known problem of semi-local functionals underestimating the band gap, the Heyd–Scuseria–Ernzerhof (HSE06)[S4] hybrid functional was employed for more accurate electronic band gap prediction. The Wannier90 package[S5] was used to make a tight-binding Hamiltonian from HSE06-level DFT calculations. This led to the creation of maximally localized Wannier functions. The WanTiBEXOS code[S6] was used to examine excitonic and optical properties, and the carbon s- and p-states were included in the orbital projections. We used two theoretical levels to calculate optical absorption spectra: the independent-particle approximation (IPA), which ignores excitonic effects, and the Bethe–Salpeter equation (BSE), which takes electron–hole interactions[S6]. The BSE calculations employed a 2D Coulomb-truncated potential with a 120 × 120 × 1 k-point grid. This simulation considers 8 conduction bands and valence bands for the description of the linear optical response in the solar emission range (0 to 4 eV). A Gaussian smearing of 0.05 eV was used to get the dielectric functions. We obtained the absorbance from the absorption coefficient, using a monolayer thickness defined as the intrinsic thickness plus a 3.3 Å van der Waals correction. We tested the solar-harvesting efficiency by determining the Shockley–Queisser (SQ) limit[S7] and the spectroscopy limited maximum efficiency (SLME)[S8] at 300 K under AM1.5G illumination[S9].

S2 Power Conversion Efficiency

Table S1: Photovoltaic performance metrics of γ-graphyne monolayer evaluated at the IPA and BSE levels compared with literature data. The spectroscopically limited maximum efficiency ($\mathrm{PCE}^{\mathrm{SLME}}$) and its maximum value ($\mathrm{PCE}^{\mathrm{SLME}}_{\mathrm{max}}$) are reported, along with the SQ efficiency ($\mathrm{PCE}^{\mathrm{SQ}}$) and the fill factor (FF), assuming a solar device operating at 300 K under AM1.5G illumination.

Optical level	$\mathrm{PCE}^{\mathrm{SLME}}$	$\mathrm{PCE}^{\mathrm{SLME}}_{\mathrm{max}}$	$\mathrm{PCE}^{\mathrm{SQ}}$	FF
γ-graphyne (IPA)	0.44	28.08	28.08	84.27
γ-graphyne (BSE)	0.41	23.84	23.84	82.29
Penta-GRA (BSE)[S10]	0.16	7.49	7.58	-
Me-GRA (BSE)[S10]	0.33	14.40	31.81	-
S-GY (IPA)[S11]	0.58	26.89	31.84	-
S-GY (BSE)[S11]	0.27	22.44	32.27	-
GDY (Exp. PCE)[S12]	10.34	-	-	72.14

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