Supporting Information

Pronounced Exciton Effects in Two-Dimensional Fullerene-based Monolayer Materials

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Supplementary Note 1: The definition of the Bethe-Salpeter Equation

While the GW approximation yields accurate quasiparticle excitation energies, it cannot reliably describe optical absorption spectra, as it accounts only for single-particle excitations. The true excited states are bound electron–hole pairs(excitons), requiring two-particle correlation function.¹

$$L(1,2;1',2') = -G_2(1,2;1',2') + G(1,1')G(2,2')$$
⁽¹⁾

Here, the notation (1) represents the combined time, spin, and spatial coordinates, i.e. $(1) = (r_1, \sigma_1, t_1)$, and G_2 is the two-particle Green's function. We also use $(x) = (r, \sigma)$ to denote spin and spatial coordinates. The electron-hole correlation function obeys a Dyson equation known as the BSE

$$L(1,2;1',2') = L_0(1,2;1',2') + \int d(3456)L_0(1,4;1',3)K(3,5;4,6)L(6,2;5,2')$$
(2)

Here, $L_0(1,2;1'2') = G(1,2')G(2,1')$ describes a non-interacting quasiparticle pair, and K is the electron-hole interaction kernel. The BSE can be written as an effective eigenvalue problem.

The BSE method computes optical properties in two steps: 1. Kernel evaluates the BSE kernel on a coarse k-point grid. 2. Absorption constructs and diagonalizes the BSE Hamiltonian to obtain exciton energies, wavefunctions, and optical spectra.²

Supplementary Note 2: Considerations on the remaining assembly configurations

In addition to the two assembled structures discussed in the main text, we also investigated several other possible assembly configurations and performed atomic embedding on those that met the convergence criteria, as shown in **Fig. S3** and **Fig. S4**. To evaluate their stability, we first considered the dynamic effects of temperature on the material structure. We found that configurations 2 and 3 underwent significant deformation and could not maintain their cage-like structures at 300 K. For configuration 1, which remained stable at 300 K (simulated using the NVT ensemble for 10 ps in AIMD), we further examined its phonon dispersion and found large imaginary frequencies, as shown in **Fig. S5**, indicating poor dynamic stability. Therefore, these three configurations are not discussed further in the main text.



Fig. S1 (a) Convergence test of the Quasi-Particle (QP) Gap calculated using the GW method, with respect to the number of empty bands and the dielectric matrix cut-off, For computational efficiency, the convergence test was conducted on a $6 \times 6 \times 1$ grid, (b) Convergence of the quasiparticle (QP) band gap obtained using a coarse K-mesh relative to the GW method. Subsequent calculations and interpolations were performed using a finer $8 \times 8 \times 1$ K-mesh., Convergence of fine kpoints with respect to the optical spectrum for (c) α -C₂₀-2D and (d) α -Mg@C₂₀-2D monolayers.



Fig. S2 (a) Structures of β -C₂₀-2D monolayer. (b) Phonon dispersion curves for β -C₂₀-2D monolayer. (c) Energy profile during AIMD simulation at 300 K for β -C₂₀-2D monolayer. (d) ELF contour plots of β -C₂₀-2D monolayer across the (001) plane. The ELF values represent the degree of electron localization, ranging from 0 (fully delocalized) to 1 (fully localized).



Fig. S3 (a) Structures of 1-C₂₀-2D monolayer. (b) Structures of 2-C₂₀-2D monolayer. (c) Structures of $3-C_{20}-2D$ monolayer.



Fig. S4 (a) Structures of 1-Mg@C₂₀-2D monolayer. (b) Structures of 2-Mg@C₂₀-2D monolayer. (c) Structures of 3-Mg@C₂₀-2D monolayer.



Fig. S5 (a) Phonon dispersion curves for 1-Mg@C_{20}-2D monolayer.



Fig. S6 (a) Structures of α -Li@C₂₀-2D, α -Na@C₂₀-2D, β -Li@-2D, β -Na@-2D monolayers, with C atoms depicted in gray, Li atoms in green, and Na atoms in yellow. (b) Phonon dispersion of α -Li@C₂₀-2D, β -Li@C₂₀-2D, α -Na@C₂₀-2D, β -Na@C₂₀-2D monolayers.



Fig. S7 PBE band structure of α -Li@C₂₀-2D, β -Li@C₂₀-2D, α -Na@C₂₀-2D, β -Na@C₂₀-2D monolayers.



Fig. S8 (a) Structures of β -Mg@C₂₀-2D monolayer. (b) Phonon dispersion curves for β -Mg@C₂₀-2D monolayer. (c) Energy profile during AIMD simulation at 600 K for β -Mg@C₂₀-2D monolayer. (d) ELF contour plots of β -Mg@C₂₀-2D monolayer across the (001) plane. The ELF values represent the degree of electron localization, ranging from 0 (fully delocalized) to 1 (fully localized).



Fig. S9 PBE band structures of monolayer (a) α -C₂₀-2D, (b) α -Mg@C₂₀-2D, (c) β -C₂₀-2D, and (d) β -Mg@C₂₀-2D.



Fig. S10 (a) Evolution of the oscillatory strength of the lowest bright exciton of α -C₂₀-2D monolayer with polarization angle. (b) the absorption edge peak of α -C₂₀-2D monolayer. (c) Evolution of the oscillatory strength of the lowest bright exciton of α -Mg@C₂₀-2D monolayer with polarization angle. (d) the absorption edge peak of α -Mg@C₂₀-2D monolayer.



Fig. S11 (a) Reciprocal space distribution of exciton wave functions in α -Mg@C₂₀-2D monolayer, the radius of the circle is proportional to $|\psi_{S}(k)|^{2}$, the pink and blue circles represent the lowest bright and dark excitons, respectively. (b) Distribution of the lowest-energy bright exciton in reciprocal and real spaces. (c) Distribution of the lowest-energy dark exciton in reciprocal and real spaces.

Monolayers	Space Group	<i>a</i> (Å)	<i>b</i> (Å)	$E_{\rm b}({\rm eV})$
α-Li@C ₂₀ -2D	Pmna (53)	5.96	10.40	-6.10
β-Li@C ₂₀ -2D	Pmmm (47)	5.70	5.81	-5.36
α -Na@C ₂₀ -2D	Pmna (53)	5.91	10.38	-6.22
β-Na@C ₂₀ -2D	Pmmm (47)	5.62	5.64	-6.91

Table S1. Summary of the geometric and electronic properties of α -Li@C₂₀-2D, β -Li@C₂₀-2D, α -Na@C₂₀-2D, β -Na@C₂₀-2D monolayers, encompassing space group symmetry, lattice dimensions (a/b), binding energy (*E*_b).

Monolayer	Carrier	$m_{x}^{*}\left(m_{0} ight)$	$m^*_{y}(m_0)$
	electron	1.61	1.01
α -C ₂₀ -2D	hole	1.88	7.14
	electron	2.40	1.00
α -Mg(a)C ₂₀ -2D	hole	3.51	0.56
	electron	1.42	1.82
β -C ₂₀ -2D	hole	0.65	0.96
	electron	0.47	0.29
β -Mg(a)C ₂₀ -2D	hole	1.02	2.50

 Table S2. Effective mass of monolayer materials.

	α-C ₂₀ -2D	α-Mg@C ₂₀ -2D	C ₆₀ -2D
$\epsilon_{\infty} ({ m meV})$	1.94	2.77	7.20
$\epsilon_{ion} (meV)$	0.07	0.12	0.18
$\varepsilon_0 (meV)$	2.01	3.89	7.38

 Table S3. Dielectric properties of monolayer materials.

Reference

- 1G. Strinati, Application of the green's functions method to the study of the optical properties of semiconductors, *Riv. Nuovo Cimento (1978-1999)*, 1988, **11**, 1–86.
- 2J. Deslippe, G. Samsonidze, D. A. Strubbe, M. Jain, M. L. Cohen and S. G. Louie, BerkeleyGW: a massively parallel computer package for the calculation of the quasiparticle and optical properties of materials and nanostructures, *Comput. Phys. Commun.*, 2012, **183**, 1269–1289.