The significant enhancement of orbital moment for the Co\textsuperscript{2+} ions is clearly presented in the integrated XMCD signal in Fig. 3(c) according to the orbital XMCD sum rule in Eqn. (1) derived by Thole et al.\cite{1}, in which the ratio between the energy-integrated XMCD signal and the energy-integrated isotropic spectra determines directly values of $L_z$ at the room temperature.

$$m_{\text{orb}} = \frac{4\int_{L_2+L_2}(\mu^+ - \mu^-)d\omega}{3\int_{S_z}(\mu^+ + \mu^-)d\omega}(10 - n_{3d}) \quad (1)$$

where $m_{\text{orb}}$ is orbital magnetic moments in the units of $\mu_B$/atom and $n_{3d}$ is the 3$d$ electron occupation number per specific cation.

The $f_{L_2+L_2}$ denotes the integration of the $L_3 + L_2$ range. The $n_{3d}$ value was estimated to be 7.21 for Co\textsuperscript{2+}, which is expected for CoO.\cite{2}

From the panel of Fig. 3(c) one can see that at RT the orbital moment is enhanced about 3 times from the STO-CFO to BFO-CFO, whereas it is slightly reduced from the BFO/CFO bilayer to CFO. Fig. 3(d) shows that Fe ions provide nearly vanishing orbital moments for all three systems. For this reason, we’ll concentrate on the magnetic properties of Co ions in order to quantitatively estimate the ordered total moment, we further calculate spin moments using the XMCD spin sum rule.\cite{3, 4}

$$m_{\text{spin}} = \frac{6\int_{L_2}(\mu^+ - \mu^-)d\omega - 4\int_{L_2+L_2}(\mu^+ + \mu^-)d\omega}{f_{L_3+L_2}(\mu^+ + \mu^-)d\omega \times (10 - n_{3d})} (1 + \frac{7<T_2>}{2<\xi_2>})^{-1} \quad (2)$$

where $m_{\text{spin}}$ is the spin magnetic moments and $<T_2>$ is the expectation value of the magnetic dipole operator. In octahedral symmetry, $<T_2>$ has been found to be negligible.\cite{5} The obtained $m_{\text{spin}}$ is listed in Table S1, where we can see a considerably large net magnetic moment in BFO-CFO as compared with that in STO-CFO heterostructures and in the BFO/CFO bilayer. Furthermore, the Fe net spin moments ($-0.19\mu_B$) are much smaller than cobalt ones for all three samples. In CoFe\textsubscript{2}O\textsubscript{4}, the Fe\textsuperscript{3+} ions at octahedral and tetrahedral sites have antiferromagnetic alignment. Therefore, they do not contribute to the net spin moment. This is consistent with our sum rule calculations and reveals that the majority of the magnetic moment for all the systems is owing to the Co\textsuperscript{2+} cations. The magnitude of the Co out-of-plane total moment is estimated as large as 2.39$\mu_B$ (2.46$\mu_B$ in-plane) for the BFO-CFO and 0.93$\mu_B$ for the STO-CFO.

Similar to SQUID, XMCD also shows that the total magnetic moment of BFO-CFO is greater than STO-CFO by 3 times in the 1 T magnetic field.

To critically check above results, we have used the sum rule of

$$m_{\text{orb}} \quad m_{\text{spin}} = \frac{L_2}{2S_{\text{sp}}^2} = \frac{2f_{L_2}\Delta\mu(E)dE}{3f_{S_z}\Delta\mu(E)dE - 2f_{L_3}\Delta\mu(E)dE} \quad (3)$$

The advantages of this sum rule are that the experimental ratio of $m_{\text{orb}}/m_{\text{spin}}$ is only related to the difference between $\mu$ and $\mu'$, namely XMCD, and this is more reliable than extracting the individual values for $L_z$ and $S_z$ since one no longer needs to make corrections for an incomplete magnetization, due to, for example, possible strong magnetocrystalline anisotropy in a polycrystalline materials and no longer needs to subtract the intensity from the edge jump. From Eqn. 3 we get $m_{\text{orb}}/m_{\text{spin}}=0.40$ which is in agreement with a ratio from the individual values for $m_{\text{orb}}=0.68$ and $m_{\text{spin}}=1.70$ from Eqns. (1) and (2), respectively.

Figure S1 XMCD spectra of Co $L_{2,3}$ (a) and Fe $L_{2,3}$ edge(b) of the BFO-CFO, STO-CFO heterostructures and BFO/CFO bilayer. The Co XMCD signal in BFO-CFO (blue curve) is large and reaches 52% at the $L_3$ edge.

Table S1. Measured out-of-plane $m_{\text{orb}}/m_{\text{spin}}$ ratio, orbital moment $m_{\text{orb}}$, spin moment $m_{\text{spin}}$ and total moment $m_{\text{total}}$ from Co XMCD spectra at room temperature for BiFe\textsubscript{2}O\textsubscript{4}, SrTiO\textsubscript{3}, CoFe\textsubscript{2}O\textsubscript{4} and BiFeO\textsubscript{3}/CoFeO\textsubscript{3} bilayer on the STO substrate.
<table>
<thead>
<tr>
<th>Magnetic moment $[\mu_B$/Co</th>
<th>BFO-CFO</th>
<th>STO-CFO</th>
<th>CFO/BFO bilayer</th>
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</thead>
<tbody>
<tr>
<td>$M/M_s$</td>
<td>0.40</td>
<td>0.38</td>
<td>0.40</td>
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<td>0.25</td>
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<tr>
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<tr>
<td>$M_{total}$</td>
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<td>0.93</td>
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**Supporting references**