Heteronuclear soliton molecules in optical microresonators

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Optical soliton molecules are bound states of solitons that arise from the balance between attractive and repulsive effects. Having been observed in systems ranging from optical fibers to mode-locked lasers, they provide insights into the fundamental interactions between solitons and the underlying dynamics of the nonlinear systems. Here, we enter the multistability regime of a Kerr microresonator to generate superpositions of distinct soliton states that are pumped at the same optical resonance, and report the discovery of heteronuclear dissipative Kerr soliton molecules. Ultrafast electrooptical sampling reveals the tightly short-range bound nature of such soliton molecules, despite comprising dissipative Kerr solitons of dissimilar amplitudes, durations and carrier frequencies. Besides the significance they hold in resolving soliton dynamics in complex nonlinear systems, such heteronuclear soliton molecules yield coherent frequency combs whose unusual mode structure may find applications in metrology and spectroscopy.

INTRODUCTION

Solitons are one of the most fascinating phenomena in nonlinear dynamics due to their universal spatial or temporal localization of wave forms and the resulting particle-like behavior [1, 2]. The ubiquity of solitons has been manifested by the numerous observations in hydraulics [3], plasmas [4], lasers [5] and Bose-Einstein condensates [6, 7], despite the drastic difference in the governing physics. First discovered in optical fibers [8], in which case losses play a negligible role, optical temporal solitons have also been observed in “open systems”, i.e. systems which exhibit dissipation [9]. In such dissipative systems solitons result from non-equilibrium driving, i.e. from a double balance of loss and gain, as well as dispersion and nonlinearity and correspond to specific solutions of spatiotemporal self-organization. One specific example is dissipative Kerr solitons (DKS), which can form in a continuous wave (CW) driven Kerr nonlinear cavity [10, 11], as mathematically described by the Lugiato-Lefever equation (LLE) [12]. With the frequency combs (also referred to as microcombs [13]) they generate, DKS have been successfully applied in spectroscopy, ranging and telecommunication [14, 19].

Like their spatial counterparts [20-22], temporal solitons can form bound pairs or groups, akin to molecules. Temporal soliton molecules have been observed in conservative systems such as optical fibers [23-24], and have also been theoretically and experimentally investigated in dissipative systems [27, 28]. Moreover, recent advances in dispersive-Fourier-transformation-based imaging techniques have revealed the formation of soliton molecules in a variety of mode-locked lasers [29, 32]. Investigation on soliton molecules provides a direct route to study the interactions between solitary waves, and the formation and dissociation of soliton molecules are closely related to subjects such as soliton collision [33], soliton splashing [34], soliton rains [35] and the trapping of solitons [36]. Besides the significance they bring to the fundamental understanding of soliton physics, soliton molecules also present the possibility of transferring optical data surpassing the limitation of binary coding [37].

To date, binding of DKS has only been possible when dispersive waves interlock multiple identical solitons [35, 40], which leads to the formation of “homonuclear” soliton molecules with long-range binding (i.e., the distances between solitons are much larger than the widths of solitons). In this work, for the first time we generate heteronuclear DKS molecules, which are stable bound states comprised of solitons with distinct carrier frequencies, pump detunings, temporal widths and soliton energies. This is achieved by pumping one resonance with a laser that is phase-modulated at a frequency that is only one thousandth of the cavity free spectral range (FSR). This pumping scheme allows us to access a multistability regime [11, 12] where multiple dynamical microcomb states coexist. Theoretically, besides the usual dispersive-wave-mediated long-range binding, we predict the unusual binding mechanism that results in the direct interaction between dissimilar solitons in close proximity. Experimentally, we apply a dual-comb sampling technique to measure the inter-soliton separation, revealing that distinct solitons can indeed form stable bound structures in systems with instantaneous nonlinear response, despite the fact that the relative phase between constituent solitons is rotating.

DISCRETELY PUMPED KERR MICRORESONATORS

In contrast to a conventional monochromatic pumping scheme, here we drive a single resonance with two laser fields, in order to simultaneously generate two distinct
Figure 1. **Generation of heteronuclear dissipative Kerr soliton molecules.** (a) Principle of the discrete pumping scheme. Closely bound dissimilar solitons are generated by pumping a single resonance with two laser fields of different frequencies simultaneously. (b) Simulated intracavity field evolution showing the formation of soliton molecules. An enlargement of the soliton binding is shown in the inset. Due to the periodicity of the fast time axis the solitons moving out of the map from the bottom will reappear from the top. More details of the simulation can be found in [43]. (c) Three typical snapshots of the field in (b) at the numbered dashed lines are displayed, corresponding to (1) coexistence of a major soliton and modulational instability; (2) coexistence of unbound dissimilar solitons; and (3) heteronuclear soliton molecule respectively. The evolution of the inter-soliton separation (indicated by the white double-arrow in the inset in (b)) is presented on the right side, showing the stabilization of the separation after oscillations. (d) Frequency comb spectra corresponding to the independent solitons pumped by the major pump (major soliton) and by the sideband (minor soliton) as well as the heteronuclear DKS molecules respectively. Comparison of the comb powers shows that the soliton molecule spectrum is the superposition of the spectra of the two dissimilar solitons.
soliton states that are each triggered by the bistability of Kerr cavities. Such complex dynamics of multi-valued stationary states, known as multistability, was recently investigated in fiber ring resonators with a single driving laser pumping two resonances [42]. Naturally, Kerr microresonators appear to be an ideal platform for studying the multistability since they are more robust against environmental perturbations and their strong nonlinearity allows for wider soliton existence range in the frequency domain. However, the small sizes of microresonators leads to very large FSRs that significantly surpass the bistable range, thus forbidding the multistability regime to be entered. Here we demonstrate that such obstacles can be circumvented by driving one resonance with two laser fields whose frequencies differ by less than the soliton existence range. Since there is only one resonance being pumped, the LLE model is adequate to describe the dynamics. Including a second pump in the driving term, we express the discrete pumping scheme as:

\[
\frac{\partial A}{\partial t} + i \sum_{j=2} D_j (\frac{\partial}{\partial \phi})^j A - i g |A|^2 A = \left( \frac{\kappa}{2} + i(\omega_0 - \omega_p) \right) A + \sqrt{\kappa_{\text{ex}}} \cdot s_{\text{in}} (1 + \frac{\epsilon}{2} e^{i \Omega t}) \tag{1}
\]

where \( A \) is the envelope of the intracavity field, \( \omega_0 \) and \( \omega_p \) are the angular frequencies of the pumped resonance and the laser respectively, \( D_j \) is the \( j \)-th-order dispersion, \( \phi \) is the co-rotating angular coordinate that is related to the round-trip fast time coordinate \( \tau \) by \( \phi = \tau \times D_1 \) (where \( \frac{D_1}{2\pi} \) is the FSR), \( \kappa \) is the cavity decay rate, \( \kappa_{\text{ex}} \) is the external coupling rate and \( |s_{\text{in}}|^2 = \frac{P_{\text{in}}}{\hbar \omega_0} \) is the driving photon flux, where \( P_{\text{in}} \) denotes the power of the main pump. Here \( g = \frac{\hbar \omega_0 \kappa_{\text{ex}}}{2\sqrt{n_0 n_2}} \) is the single photon induced Kerr frequency shift, where \( n_0 \) and \( n_2 \) are the refractive and nonlinear optical indices, \( V_0 \) is the effective mode volume, and \( \epsilon \) is the speed of light. Moreover, \( \epsilon \) is the modulation index for generating the blue-shifted sideband from a phase modulator, e.g. an electrooptic modulator (EOM), and \( \frac{\kappa}{2} \) represents the sideband offset frequency, which is set to be positive to reflect the blue-shifted frequency.

Our theoretical analysis shows that the discrete pumping can simultaneously generate two different soliton states, which can be approximated by the superpositions of solitons excited by only the main pump and by only the sideband, respectively (see Supplemental Material [43] for details). Here we note that our discrete pumping scheme is fundamentally different from bichromatic pumping methods investigated in previous studies [42, 47]. First, while the second pumps in previous works were all offset from the main pump laser by approximately one or multiple FSRs, the offset we apply here is only 12 - 30 MHz, i.e. approximately a thousandth of the FSR (14.09 GHz). Second, the bichromatic pumping scheme was used for modulating the intracav-ity CW background to manipulate the spatiotemporal characteristics of the otherwise ordinary monochromatically pumped microcombs. In contrast, the modulated laser in this work generates two dissimilar sets of microcombs, each of which would still exist in the absence of the other’s drive.

The simulated formation of heteronuclear soliton molecules is presented in Fig.1(b). As the two pumps are swept towards lower frequencies across a resonance, the major pump excites modulational instability (MI) at first, followed by DKS formation. Next, the minor pump scans across the same resonance to generate its microcombs while the major pump is supporting the major DKS. After the minor solitons are formed, due to self-frequency-shifting effects such as high-order dispersion (in this study) and Raman scattering, the major and the minor DKS travel with different group velocities, until the two solitons are close, with a separation where an equilibrium is achieved. Such equilibrium is obtained when the soliton group velocity difference is balanced with the inter-soliton “repulsion” caused by cross phase modulation (XPM) (see [43] for details). Intuitively, in Kerr microresonators where the nonlinear response is instantaneous and local, one may expect that discretely driven solitons can not bind because the Kerr nonlinearity-mediated effect [24] averages out as the relative phase between two distinct solitons is constantly rotating, given that the solitons have different carrier frequencies. Indeed, a fixed phase difference between similar solitons (and their oscillatory tails) is essential to the formation of multi-soliton long-range bound states [38, 40]. Even in a broader perspective that includes spatial solitons, when the relative phase between driving fields is not fixed (e.g. incoherent solitons and vector solitons), bound states can be formed only when the system’s nonlinearity has a non-instantaneous or nonlocal nature [48-50]. In our work the XPM effect creates a refractive index barrier to stop solitons of different carrier frequencies (and hence difference group velocities) from colliding. As a result, heteronuclear soliton molecules are formed, with a final group velocity that lies in between the native velocities of the two DKS respectively, according to the conservation of momentum (see [43] for details).

The corresponding frequency comb spectra are presented in Fig.1(d). Because the major and the minor solitons are of different carrier frequencies, the coarsely resolved comb spectra of heteronuclear molecules acquired by an optical spectrum analyzer (OSA) do not show interference patterns that are typical of monochromatically pumped multi-soliton states [51]. Rather, the averaged comb spectrum of the heteronuclear DKS molecules is the linear superpositions of the spectra of the major and the minor DKS.
Figure 2. Observation of dissipative Kerr soliton molecules. (a) The schematic experimental setup. (b) The generated comb power as the laser is frequency swept across a resonance. The red-shaded area is the comb power generated by the major pump, while the blue-shaded area indicates the power of the comb driven by the blue-shifted minor pump. (c) The spectrum of the DKS molecule that is composed of major-single-DKS and minor-single-DKS. (d) The measured response of VNA with modulation probing technique. (e) - (f) Spectra of DKS combs driven by only the major pump and by only the minor pump respectively. The red traces are the sech fittings. The sum of the two fittings is plotted in (c).

EXPERIMENTAL GENERATION OF HETERONUCLEAR SOLITON MOLECULES

We generate heteronuclear DKS molecules in a magnesium fluoride (MgF₂) whispering-gallery-mode resonator (WGMR). The experimental setup is depicted in Fig.2(a) (see [43] for more details). Fig.2(b) shows the generated microcomb power as the laser frequency sweeps across a resonance. By scanning the laser frequency into the DKS molecule regime, we observe the spectrum of the superposed microcomb of major-single-DKS and minor-single-DKS states (Fig.2(c)), while Fig.2(e) and (f) show the spectra of the monochromatically pumped single-DKS states driven by the major and the minor pumps respectively. Dynamical probing with vector network analyzer (VNA) [52] measures the radio-frequency (RF) spectrum of the transfer function in Fig.2(d). We observe two sets of the typical double-resonance features that are induced by the soliton resonance (“S-resonance”) and the CW resonance (“C-resonance”) [52], showing that the molecule spectrum is indeed the superposition of two monochromatically driven DKS spectra.

We excite a variety of comb patterns of different compositions, which are presented in Fig.3 with the corresponding simulated spectra, showing remarkable agreement. For all the comb patterns we observe only one repetition rate of the out-coupled soliton trains, indicating that the coexistences of solitons are truly bound states. Again, we note that the superposed comb spectra do not give information on the separations between the major solitons and the minor solitons in a bound state.

STRUCTURE OF SOLITON MOLECULES

Since the observed comb spectrum indicates that the generated solitons are inevitably impacted by high-order dispersion and mode-crossing-induced dispersive waves, the DKS repetition rate ($f_{\text{rep}}$) depends on the effective pump-resonance detuning [53, 54]. Consequently, the major and the minor DKS should have different $f_{\text{rep}}$ because of their different detunings (major detuning $\delta_1 = \frac{\omega_0 - \omega_p}{2\pi}$ and minor detuning $\delta_2 = \delta_1 - \frac{\Omega}{2\pi}$) when one assumes that there is no interaction between them. Such assumption, however, is false. Because the major and the minor solitons share the same optical mode family (i.e., whispering gallery modes with the same polarization and identical radial and polar numbers), they would either
Figure 3. **Optical spectra of coexistence of distinct solitons.** Experimentally measured (left column) and numerically simulated (right column) spectra of soliton coexistences composed of: (a) and (f) major single-DKS and minor dual-DKS; (b) and (g) major dual-DKS and minor single-DKS; (c) and (h) major dual-DKS and minor dual-DKS; (d) and (i) major single-DKS and minor triple-DKS; (e) and (j) major single-DKS and minor MI. The relative positions of the major solitons (red dots) and the minor solitons (blue dots) are qualitatively depicted on the right side of the simulation panels. For all the simulations the sideband modulation frequency is set to be 18 MHz and the pump laser detuning is set to be 24 MHz, except for the superposition of major soliton state and minor MI the pump detuning is 17.7 MHz.

The repetition rate difference ($\Delta f_{\text{rep}}$) between the EOC and the soliton microcombs is set to be $\sim 30$ MHz. As shown in Fig. 4(b), (c), (e) and (f), the sampled inter-

To verify this prediction, we adopt the imaging technique [34] with an electrooptic comb (EOC) to examine the bound structures. The setup is displayed in Fig. 4(a). For DKS generation the pump-resonance detuning is stabilized by implementing the Pound-Drever-Hall (PDH) laser locking technique with an EOM as a phase modulator. The major pump frequency is locked to the high-frequency PDH sideband, thus locking the detuning ($\omega_0 - \omega_p$) to be equal to the PDH modulation frequency of 25 MHz. The carrier frequency of the EOC is different from the soliton pump laser frequency by $\sim 5.5$ GHz. The repetition rate difference ($\Delta f_{\text{rep}}$) between the EOC and the soliton microcombs is set to be $\sim 30$ MHz. As shown in Fig. 4(b), (c), (e) and (f), the sampled inter-

have different $f_{\text{rep}}$ and show soliton collisions, or have the same $f_{\text{rep}}$ by forming bound states, i.e., heteronuclear DKS molecules. As predicted by our simulation and supported by the single repetition rate of superposed microcombs, the dissimilar solitons travel with same group velocity, likely with a small inter-soliton separation.

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Figure 4. **Electrooptic examination of the structures of heteronuclear DKS molecules.** (a) The experimental setup and the optical spectrum of the electrooptic comb. The first EOM serves as the phase modulator for generating PDH error signals in order to lock the pump-resonance detuning. (b) - (g) The optical spectrum (b, e), the sampled interferograms (c, f) and the simulated temporal profiles (d, g) of the major-single-with-minor-single and the major-single-with-minor-dual superposed microcombs respectively. (h) - (j) The RF spectrum of the interferograms of the major-single-with-minor-dual DKS molecules and the separated spectra of the major DKS and the minor DKS respectively. (k) The separated interferograms of the microcomb in (e). (l, m) The envelopes (in absolute values) of the separated interferograms of the major-single-with-minor-dual and the major-single-with-minor-single DKS molecules respectively. The inferred real-time separations between the major DKS and the minor DKS are indicated by double-arrows in (d), (g), (l) and (m).

Interferograms show only one repetition period, once again showing that the two constituent microcombs have the same $f_{\text{rep}}$. However, due to the limited spectral span of the EOC and the chirping of DKS which is introduced by the notch filter, the interferogram duration is typically above 2 ns, which leads to a temporal resolution that is much broader than the inter-soliton separations between dissimilar DKS, thus potentially forbidding us from uncovering the bound structures. Nevertheless, we use fast Fourier transform (FFT) to transform the sampled interferogram streams of the major-single-with-minor-dual DKS microcomb into the RF spectrum (Fig.4(b)). Because the major DKS and the minor DKS have different $f_{\text{ceo}}$, we are able to decompose the RF spectrum into the major-DKS components (Fig.4(i)) and the minor-DKS components (Fig.4(j)). Then we apply inverse FFT to...
Figure 5. **Coexistence of long- and short-range binding mechanisms.** (a) Schematic illustration of the coexistence of long-range (dispersive-wave-mediated) and short-range (XPM-induced) binding mechanisms. (b) Dispersion used in the simulation. At mode number of 60 the resonance frequency has a large deviation (shown in red circle) to produce intensive single-mode dispersive wave. The inset displays the comb spectrum, which shows the single-mode dispersive wave in red. (c) Simulated evolution of the bound state of 1 major soliton and 2 minor solitons with the dispersive-wave-mediated binding. (d) Simulated evolution of 1 major soliton and 2 minor solitons without introducing dispersive waves.

For heteronuclear soliton molecules that are of multiple major or minor solitons, the situation is more complicated as the binding between similar solitons relies on interlocking via dispersive waves. Indeed our simulations reveal that the coexistence of the short-range binding due to the XPM effect and the long-range binding caused by the dispersive-wave-mediated effect is essential for the formation of complex molecules beyond the basic form of single major soliton with single minor soliton. Fig.5(a) depicts the concept of such combined binding mechanism. Fig.5(b) shows the resonator dispersion used in the qualitative simulation. In order to introduce dispersive wave effect we add large frequency deviation to the resonance with mode number of 60. As can be seen from the inset of Fig.5(b), such resonance frequency deviation generally leads to enhancement of the comb power in the mode, e.g. a single-mode dispersive wave. The simulation is started with a major soliton and two minor solitons seeded in the intracavity field. Fig.5(c) shows the evolution of the solitons. After the major soliton is bound with one of the minor solitons, the other minor soliton that is well separated from the bound pair also changes its soliton group velocity due to the long-range binding connecting the minor solitons. Consequently the three solitons travel with the same velocity, becoming a complex bound group. To stress the unique role of the dispersive wave, we repeat the simulation without the long-range binding, the second minor soliton moves with its original velocity after the first minor soli-
Figure 6. Mutual coherence of soliton molecule. (a) An ultrastable-cavity-locked laser beats with a pair of comb teeth that is 20 FSRs away from the pumped resonance (optical resonances are shown as the gray Lorentzian shapes). The beat frequencies are mixed down to \( f_1 \) and \( f_2 \) at low frequency range for frequency counting. (b) The RF spectrum of the mixed-down signals, with resolution bandwidth (RBW) of 10 kHz. The frequency difference between \( f_1 \) and \( f_2 \) is 22 MHz, which is equal to the sideband offset frequency \( \frac{\Omega}{2\pi} \) in the experiment. The weak peak at 44 MHz is the second order harmonic of the EOM modulation frequency. The inset is the repetition rate spectrum of the soliton molecules, showing only one frequency at 14.093 GHz. (c) Calculated Allan deviations of stabilized \( f_1 \) and \( f_2 \), showing almost identical frequency stabilities. The error bars are included but not visible in the figure due to their extremely small amplitudes.

In Fig. 6(g) we plot the simulated profile of the complex molecule that is corresponding to the experimental observations shown in Fig. 4(g) and (f). Again, the inter-soliton separation between the major and minor solitons is in excellent agreement with the measured value.

**FREQUENCY COHERENCE MEASUREMENT**

Despite the frequency offset imposed by the driving lasers, the binding of the solitons mutually locks the repetition rates, thus potentially giving rise to a high frequency coherence between the major and the minor DKS microcombs. To test the coherence, we use a 1553-nm laser whose frequency is stabilized to an ultrastable Fabry-Perot cavity to measure the frequencies of a pair of major and minor comb teeth that is 20 FSRs (~2.3 nm) apart from the pumped resonance. The experimental scheme is illustrated in Fig. 3(a). The RF spectrum of the beat signals (see Fig. 4(b)) shows two frequencies that differ by the exact value of the EOM modulation frequency which was set to be 22 MHz in this experiment. We also fully stabilize the microcomb (see SI for details) and then count the two down-mixed beat signals \((f_1 \text{ and } f_2)\) at the same time and the recorded frequencies allow us to confirm unambiguously that the frequency of the minor comb is offset from the frequency of the major comb by \( \frac{\Omega}{2\pi} \). The Allan deviations of the two frequencies are displayed in Fig. 4(c), showing almost identical instabilities. We attribute the imperfect overlap of the Allan deviations to the imperfect synchronization of the counter gating, as well as the fluctuation of the pulse separation in soliton molecules \([55]\) and the internal motion of soliton molecules \([30]\). The in-depth analysis of the fluctuations of inter-soliton separations is beyond the scope of this work. Nevertheless, we emphasize here that the frequency coherence the DKS molecule comb exhibited is already sufficient for a wide range of applications in frequency metrology.

**CONCLUSION AND DISCUSSION**

We use modulated light to enter a novel multistability regime in a Kerr microresonator to generate heteronuclear soliton molecules. The structures of the soliton molecules, as well as the underlying mechanisms that enable the formation of such new DKS bound states are analyzed experimentally and numerically. The mutual frequency coherence of the generated combs is verified with both spectral analysis and frequency counting.

For practical applications, comb-based sensing and metrology may benefit from heteronuclear DKS molecules that provide an additional coherent comb. In particular, with the feature that the major comb and the minor comb are highly coherent despite the fact that they share no frequency components, the heteronuclear solitons can be used with the interlocking of counter-propagating solitons \([56]\) to generate ultrahigh coherent dual-comb spectrometer without the overlapping of comb teeth (thus no RF spectrum folding).
Furthermore, soliton bound states have been used for optical data buffers \cite{10}, and it has been proposed to use soliton molecules in optical telecommunication to break the restriction of binary coding \cite{37}. Naturally one would expect the DKS molecules to be capable of storing and buffering soliton-molecule-based data.

Data availability statement The data used to produce the results of this manuscript will be available on Zenodo upon publication.

Authors contributions W.W. conceived the concept and the experimental setup, developed theoretical analysis, and performed numerical simulations. W.W. and R.B. performed the experiments and analyzed the data with assistance from E.L.. E.O. and T.H. constructed the analysis, and performed numerical simulations. W.W. and T.J.K. supervised the project.

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SUPPLEMENTAL MATERIAL

DETAILS OF EXPERIMENTAL SETUP FOR SOLITON GENERATION

The MgF$_2$ WGMR is fabricated from a z-cut a crystalline disk with diamond shaping and surface polishing techniques. The output power of a 1555-nm laser is amplified by an Erbium-doped fiber amplifier (EDFA) to $\sim 300$ mW and an EOM is driven by a sine-wave signal output by a function generator to generate optical sidebands. A tapered fiber that is in contact with the WGMR is used to couple light into the resonator. The loaded quality-factor ($Q$) of the mode resonance that generates combs in our work is measured to be $\sim 1 \times 10^9$, corresponding to a resonance bandwidth ($\kappa/2\pi$) of 200 kHz. The transmitted light is filtered with fiber Bragg grating notch filters to suppress the intensive pump light and then registered by a photodetector.

To generate DKS molecules, an arbitrary function generator (AFG) is used to sweep the laser frequency linearly. A sine-wave signal with frequency of 12 - 30 MHz produced by a second AFG is applied to the EOM to generate optical sidebands of the pump laser. We set the modulation index $\epsilon$ to be $\sqrt{2}$, i.e., the power of the first order sideband is half of the main pump power. Once the DKS molecules are generated, because of the self-thermal-stabilization in the DKS regime, we can maintain the molecule state for up to a few minutes without any active control measures. With active frequency locking applied to the effective detuning, the DKS molecule state can be sustained indefinitely.

DETAILS OF INTER-SOLITON SEPARATION ANALYSIS

After the soliton molecules are generated, the microcomb is beaten with the EOC on a fast photodetector to generate interferograms and the output of the photodetector is recorded by a ultrafast oscilloscope for further analysis.

For the major-single-with-minor-single molecules shown in Figure 4(b and c), the sampling rate of the oscilloscope was set to be 20 GHz/s. Data of 2 ms was recorded, which includes $4 \times 10^7$ data points, corresponding to approximately $6 \times 10^4$ interferograms. We use the method described in the main text to separate the interferograms of major solitons and minor solitons respectively in the time domain, and then locate the positions of maximum intensity of each interferogram to determine the inter-soliton separations. The averaged inter-soliton separation is 512 fs, with a standard deviation of 79.5 fs (15.5% of the separation value).

For the major-single-with-minor-dual molecules shown in Figure 4(e and f), the sampling rate was set to 40 GHz/s and data of duration of 0.5 ms was recorded, which comprises $\sim 1.5 \times 10^4$ interferograms. Using the same approach we determine the averaged separation between the major soliton and the minor soliton to be 795 fs, with a standard deviation of 37.4 fs (4.7% of the separation value).

The analysis above shows that the resolution of the electrooptic sampling technique is not limited by the pulse width of the probing EOC, and that by increasing the data acquisition rate the accuracy can be further improved. However, one should note that the sampling technique is not capable of accurately characterizing the width or the amplitude of individual soliton. Since the EOC has only $\sim 43$ comb teeth, in the frequency domain it can only sample a very limited spectral range of the microcombs. Consequently, while the interferograms can be used to determine the temporal locations of the maximum intensity of solitons, they do not yield the correct pulse widths. And because in the frequency domain the major solitons are more powerful than the minor solitons mostly in terms of the wider spectral span, the central frequency components of the major and the minor solitons sampled by the EOC are very similar in field amplitude. As a result the amplitudes of interferograms of major solitons and minor ones are almost the same, which is exactly what we observed in Figure 4(k, l and m).

SIMULATIONS

The LLE-based simulations are performed with split-step technique. Adaptive-step-size Runge-Kutta method is utilized to carry out the numerical simulations. For all simulations the optical mode intrinsic resonance bandwidth is set to be 100 kHz and the critical coupling condition is chosen. To faithfully reproduce the experimental conditions in this work, both the blue-shifted and the red-shifted first-order sidebands generated by the EOM are added to the pump source.

In generating the results presented in Figure 1 in the main text, artificial perturbations to the intracavity field were made during the laser scanning process in order to obtain the state of single-major-and-single-minor DKS at the end of the scanning. The optical comb spectra of major-DKS-only and minor-DKS-only states are simulated by
allowing only the corresponding DKS to exist. The superposed DKS microcomb spectrum is calculated by averaging the immediate comb spectrum for several photon decay times.

In simulating the various superposed comb spectra presented in Figure 3 in the main text, we use seeded field profiles with fixed detunings instead of arbitrary DKS comb patterns that grow from MI and chaotic states during detuning scanning. Fig. S.1 shows the simulated temporal profiles of the intracavity intensity that correspond to the simulated comb spectra presented in Figure 3 in the main text. Second-order dispersion coefficient $D_2 = 2 \text{kHz}$ is used in the simulation, while higher-order dispersion is excluded to maintain the inter-soliton separations exactly as seeded to faithfully reproduce the experimental observations. This approach, unfortunately, eliminates the difference in group velocities of the major and the minor DKS. Nevertheless, since the interference patterns of the optical spectra are determined by the inter-soliton separations between identical solitons (in either major multi-soliton states or minor multi-soliton states) and the inter-soliton separations between dissimilar DKS do not influence the averaged comb patterns at all, this approach allows us to achieve excellent agreement between the experiments and the simulations. Alternatively, we can add single-mode dispersion deviations to the cavity dispersion to simulate the mode-crossing-
induced single-mode dispersive waves in order to create binding between identical solitons driven by the same pumps. Then with third-order dispersion we can show simulated heteronuclear soliton molecules that are composed of distinct solitons and multiple identical solitons (like Figure 4(g) in the main text). In that case, however, the excellent agreement between the simulated and the measured comb spectra is difficult to achieve, as the temporal separations between identical solitons are difficult to control precisely. The reason is that in the experiments the comb shows multiple mode-crossing-induced dispersive waves that are difficult to accurately describe in the simulation.

For the soliton positions qualitatively illustrated in the insets of Figure 3, we use the results obtained from the investigation on the bound structures so the major and the minor solitons are closely bound.

To simulate the temporal profiles of the soliton molecules shown in Figure 4 in the main text, we add the third-order dispersion coefficient $D_3 = -4\text{ Hz}$ to the cavity dispersion. Moreover, we include mode crossing effect for the single-major-with-dual-minor-DKS state shown in Figure 4(g). The mode crossing effect produces single-mode dispersive wave emission from mode of $u = 30$ (central mode number $u = 0$) that fixes the separation between the two minor solitons.

**DETECTION RANGES OF SOLITON MOLECULE EXISTENCE**

We use the LLE model to determine the detuning ranges where stable heteronuclear soliton molecules can exist. The effective major detuning ($\Delta_1 = 2\pi\delta_1$) is changed from $40\kappa$ to $130\kappa$ with step of $10\kappa$ and the effective minor detuning ($\Delta_2 = 2\pi\delta_2$) is tuned continuously to find the critical values where the soliton molecules disintegrate or the solitons annihilate.

Fig. S.2 summarizes the simulation results. We find that for a fixed major detuning, there is a maximum minor detuning (red circles) beyond which the soliton molecule state will annihilate due to the constituent solitons’ annihilation. Therefore there is a minimum value for the sideband offset frequency $\Omega$. In our experiment we found that the minimum $\Omega$ for molecule generation is around 12 MHz, which agrees relatively well with the simulation (see Fig. S.3). When $\Delta_2$ is approximately below 9.5$\kappa$, the minor soliton starts to breathe, and will eventually annihilate when $\Delta_2$ is below $\sim 8.5\kappa$ (blue squares). This behavior is just like the typical monochromatically pumped soliton breathers with a small detuning. Interestingly, when $\Delta_1$ is above 80$\kappa$, there is a critical value of minor detuning (yellow diamonds) below which the major solitons and the minor solitons detach from each other but both exist. Consequently, in the blue shaded range the minor and the major solitons coexist but the stable bound states of heteronuclear molecules cannot form anymore. We suspect that the reason is that as the difference between $\Delta_1$ and $\Delta_2$ becomes larger the unperturbed group velocity mismatch is larger, which will eventually overcome the repulsive force. However, in the experiment we never observed such molecule disintegration.

Figure S.2. Simulated detuning range for the existence of heteronuclear soliton molecules. (a) The red-shaded range is where stable heteronuclear soliton molecules can exist. In the blue shaded range both the major and the minor solitons coexist, but the stable bound states of heteronuclear soliton molecules cannot be formed anymore. As a result, the major solitons and the minor solitons travel with different group velocities. (b) Intracavity field amplitude evolutions of two examples: soliton coexistence only (upper figure, major detuning $\Delta_1 = 120\kappa$, minor detuning $\Delta_2 = 10\kappa$) and heteronuclear soliton molecule (lower figure, $\Delta_1 = 120\kappa$, $\Delta_2 = 30\kappa$).
Figure S.3. **Soliton power spectra with different sideband modulation frequencies in soliton molecule generation.** By varying sideband modulation frequency the soliton coexistence (molecule) range is experimentally examined. When the modulation frequency is below $\sim 12$ MHz the major soliton “steps” after the MI stage does not show anymore (indicated by the red box), which means that the minimum $\Omega$ is approximately equal to $60\kappa$.

We also try different third-order dispersion $D_3$ in the simulation and we find that with other parameters (pump powers, detunings, FSR, etc.) kept the same as those used for the simulations for the main text, when $|D_3| < 4$ Hz stable soliton molecules can always be formed. When $|D_3| > 5$ Hz the soliton molecules are not stable anymore as the molecules can disintegrate or one of the solitons will annihilate.

Although we do not intend to explore the full parameter space for soliton molecule existence as the involved parameters are too many, which makes the thorough investigation on this direction beyond the scope of this work, we test with varied pump powers and the simulation results show that when the minor pump power is approximately a factor of 8 higher than the major pump power the major soliton in the molecule annihilates. However, experimentally we find that the minor pump power needs to be kept below $\sim 70\%$ of the major pump power in order to generate soliton molecules. The in-depth study for this observation is to be carried out in the future.

**DYNAMICAL BRANCHES OF DISCRETELY PUMPED MICROCOMBS**

In this section we compare simulations based on discrete pumping with conventional LLE model with monochromatic pumping, and analyze the branches of multistability with the simulation results. We perform numerical simulations based on Eq.1 in the main text as the main pump and the blue-shifted sideband are swept over an optical mode resonance. The sideband modulation frequency $\Omega$ is fixed to be $90\kappa$, and only second-order dispersion $D_2 = 2$ kHz is included in the cavity dispersion for the simulations. The simulated evolution of the intracavity field amplitude is presented in Fig.S.4(a), showing the coexistence of major DKS and minor MI state as well as the coexistence of major DKS and minor DKS. Without higher-order dispersion both major and minor DKS have the same group velocity, therefore no heteronuclear DKS molecules are formed due to the lack of restoring force. In Fig.S.4(b) we plot the peak value of $|A|^2$ of both the major DKS and the minor DKS in green traces. The regimes of coexistence of distinct comb states are marked in the figure too.

We assume that the soliton solutions to Eq.1 in the main text can be approximated in the form of superpositions of the soliton solutions to the conventional LLE model driven by only the major pump and by only the sideband respectively, i.e., there is no interaction between dissimilar solitons and to an individual soliton state a driving field of a different frequency is merely a perturbation whose effect can be reasonably ignored. Hence we can express the discrete-pumping scenario with two independent LLEs:

$$\frac{\partial A}{\partial t} - \frac{\kappa}{2} D_2 \frac{\partial^2 A}{\partial \phi^2} - i g |A|^2 A = \left( \frac{\kappa}{2} + i(\omega_0 - \omega_p) \right) A + \sqrt{\kappa_{ex}} \cdot s_{in}$$  \hspace{1cm} (S.1)
Figure S.4. **Comparison of numerical simulations based on single LLE with discrete pumping scheme and two independent conventional LLEs.** (a) Evolution of the intracavity field amplitude as the laser frequency is swept across an optical resonance. Between the dashed lines the coexistence of major DKS state and minor MI state appears at first, followed by the coexistence of major DKS (dual-soliton state) and minor DKS (9-soliton state). In the region where the major solitons and minor MI coexist, the locations of major solitons fluctuate heavily and some of them annihilate due to the influence of the minor MI. (b) Comparison of simulated $|A|_{\text{max}}^2$ for the major DKS and the minor DKS based on Eq.1 in the main text and based on Eq.S.1 and Eq.S.2 respectively. The stable (unstable) branches of the CW steady state is also shown in red solid (dashed) curves. Superpositions of major DKS and minor MI can exist in the orange-shaded detuning range and the superpositions of major DKS and minor DKS can be generated in the purple-shaded range.

\[
\frac{\partial A}{\partial t} - \frac{1}{2} D_2 \frac{\partial^2 A}{\partial \phi^2} - ig|A|^2 A = \left( -\frac{\kappa}{2} + i(\omega_0 - \omega_p - \Omega) \right) A + \sqrt{\kappa_{ex}} \cdot s_{sb} \tag{S.2}
\]

where $|s_{sb}|^2$ is the power of the sideband. We plot the CW steady-state solutions to Eq.S.1 and Eq.S.2 in Fig.S.4(b) in red traces. Next we carry out numerical simulations based on the two independent equations with the same laser sweeping speed and range. We plot the corresponding $|A|_{\text{max}}^2$ of the major and the minor states in Fig.S.4(b) in blue traces. One can see that the two sets of simulations agree very well in terms of the generated microcomb power and the detuning range for soliton microcomb existence. The discrepancy of the power fluctuations simulated with Eq.1 in the main text around $\Delta_1 = 100\kappa$ indicates that the MI state of the minor comb introduces power instabilities of the major DKS state. Understandably, such interactions between the two comb states cannot be described by the independent LLEs, in spite of the qualitative agreement they yield.

**SOLITON BINDING MECHANISM**

Conventionally the soliton binding mechanism is explained as the balance between the attractive and repulsive forces between two closely located solitons. Here we aim to provide an intuitive explanation on the physical mechanisms behind the forces, although a detailed quantitative analysis is beyond the scope of this work.

On the one hand, in the dissipative system with discrete drives, the major solitons and the minor solitons have different group velocities in the microresonator, which would close the temporal gap between the two solitons after some time. On the other hand, as the two solitons are getting closer to each other, the field overlap between them starts to become significant. In monochromatically driven dissipative systems or in conservative systems, the relative
phase between two adjacent solitons is fixed, therefore via the Kerr effect the field overlap provides an inter-soliton force, whose amplitude and direction depend on the inter-soliton separation. In other words, the field of one of the solitons functions as a potential well to exert force on the other. In our system, however, since the relative phase between the major soliton and the minor soliton is continuously rotating with a frequency of the sideband modulation frequency $\Omega$ (see Fig. S.5), when the inter-soliton separation does not change, one may expect the time-averaged force due to relative-phase-related effects to vanish, which leaves the intensity-related effect, e.g. the cross phase modulation (XPM) to be the reason for the dominant mechanism.

Figure S.5. **Phase evolution of heteronuclear soliton molecule.** (a) The evolution of the phase of intracavity field relative to the phase of the major pump field over two modulation periods (1556 round trips). The fast time locations of the major soliton and the minor soliton are around 14.4 ps and 15.6 ps respectively. (b) The map of the normalized soliton molecule field amplitude. (c) The blow-up of the phase evolution around the soliton molecule locations.

In our proof-of-principle simulation we treat the fields driven by the major and the minor pumps separately with two individual LLEs, with intensity-related terms to depict the XPM effect between the two fields of the same polarization [58]. The coupled LLEs are written as:

\[
\frac{\partial A_1}{\partial t} + i \sum_{j=2} \frac{D_j}{j!} \left( \frac{\partial}{\partial \phi} \right)^j A_1 - ig(|A_1|^2 + 2|A_2|^2)A_1 = \left(-\frac{\kappa}{2} + i(\omega_0 - \omega_\rho)\right) A_1 + \sqrt{\kappa_{ex}} \cdot \sin \tag{S.3}
\]

\[
\frac{\partial A_2}{\partial t} + i \sum_{j=2} \frac{D_j}{j!} \left( \frac{\partial}{\partial \phi} \right)^j A_2 - ig(|A_2|^2 + 2|A_1|^2)A_2 = \left(-\frac{\kappa}{2} + i(\omega_0 - \omega_\rho - \Omega)\right) A_2 + \sqrt{\kappa_{ex}} \cdot \frac{\epsilon}{2} \sin \tag{S.4}
\]

where $A_1$ and $A_2$ are the intracavity field envelopes of the major-pumped field and the minor-pumped field respectively. This model, of course, is a simplified model that neglects other phase-dependent coupling terms between the two fields. Here we note that such simplification can be justified due to the carrier frequency difference between the two distinct soliton fields. As can be seen from Fig. S.5, the relative phase rotation period is much shorter than the time scale of the cavity photon decay time or the time for a soliton to pass by a soliton that is of different carrier frequency. Therefore it is reasonable to assume that the effects due to phase-dependent terms are mostly averaged out.

We simulate the evolutions of $A_1$ and $A_2$ based on the coupled LLEs with seeded solitons. Fig. S.6(a) and (b) show the results. In comparison with the simulation result based on a typical single LLE (shown in Fig. S.6(c)), one can
see that the coupled LLEs yield almost identical soliton molecule formation process. In Fig. S.6(d) we also plot the intracavity field amplitudes at the end of the simulations when the heteronuclear soliton molecules are formed. The comparison shows that the inter-soliton separation derived by the coupled LLEs is slightly larger than that calculated with the single-LLE model. The discrepancy is mostly likely caused by the simplified coupling mechanism described by the coupled LLEs, which ignores all the phase-related coupling terms. Yet, the simulation captures the dominant role of XPM in creating the “repulsion” that enables the binding between distinct solitons.

![Figure S.6. Comparison between single-LLE model and the model of coupled-LLEs.](image)

**REPETITION RATE OF DKS MOLECULES**

Analytical expression of the repetition rate of DKS in optical microresonators with third-order dispersion has been derived with asymptotic analysis based on method of moments [53]. Here we use the results in that study to derive \( f_{\text{rep}} \) of heteronuclear DKS molecules in resonators with third-order dispersion.

Based on the analysis in [53], when monochromatically pumped, the repetition rate shifts of the major and the minor DKS due to the third-order dispersion (\( \Delta f_1 \) and \( \Delta f_2 \)) can be respectively expressed as:

\[
\Delta f_1 = \frac{\delta_1 D_3}{3D_2} \tag{S.5}
\]

\[
\Delta f_2 = \frac{\delta_2 D_3}{3D_2} \tag{S.6}
\]

where \( \delta_1 = \frac{\omega_0 - \omega_p}{\Delta} \) and \( \delta_2 = \delta_1 - \frac{\Omega}{2\pi} \) are the pump detunings respectively, and \( D_2 (D_3) \) is the second-order (third-order) dispersion coefficient.

When a heteronuclear DKS molecule is formed by a major soliton and a minor soliton, the constant velocity as well as the repetition rate shift of the DKS molecule (\( \Delta f_3 \)) satisfy the conservation of soliton momentum, which can be written as:

\[
E_3 \Delta f_3 = E_1 \Delta f_1 + E_2 \Delta f_2 \tag{S.7}
\]
where $E_1$, $E_2$ and $E_3$ are the energies of corresponding solitons/molecules. With the approximation of the field of solitons $[53]$, soliton energy is proportional to the square root of the effective detuning ($E_{1,2} \propto \sqrt{\delta_{1,2}}$). Therefore the repetition rate shift of DKS molecules can be expressed as:

$$\Delta f_3 = \frac{E_1\Delta f_1 + E_2\Delta f_2}{E_1 + E_2} = \frac{D_3}{3D_2}(\delta_1 + \delta_2 - \sqrt{\delta_1\delta_2}) \quad (S.8)$$

We perform numerical simulations to verify the theory derived above at three different major detunings ($90 \times \frac{\kappa}{2\pi}$, $110 \times \frac{\kappa}{2\pi}$ and $130 \times \frac{\kappa}{2\pi}$) with minor detuning varied from $20 \times \frac{\kappa}{2\pi}$ to $50 \times \frac{\kappa}{2\pi}$. We set the dispersion by using $D_2 = 2$ kHz and $D_3 = -4$ Hz. By fitting the motions of DKS molecules we derive $\Delta f_3$ of DKS molecules. The numerical results are presented in Fig. S.7 in circles, triangles and diamonds. The theory are plotted in curves, showing good agreement. The increased discrepancy as the major detuning increases is attributed to the approximation used in $[53]$.

**Figure S.7.** Numerical simulations (circles, triangles and diamonds) and theoretical calculations (curves) of the repetition rate shift of heteronuclear DKS molecules. As denoted in the figure, three different major detunings of $90 \kappa$, $110 \kappa$ and $130 \kappa$ are used for simulations respectively.

**FREQUENCY COHERENCE MEASUREMENT DETAILS.**

A 1553-nm laser whose frequency is stabilized to an ultrastable (relative frequency instability $< 1 \times 10^{-13}$ at integration time of 1 s) Fabry-Perot cavity to measure the frequencies of a pair of major and minor soliton comb teeth that is 20 FSRs ($\sim 2.3$ nm) apart from the pumped resonance. We also frequency-stabilize the superposed microcomb to a fully stabilized fiber-laser-based frequency comb by frequency-locking the effective detuning with Pound-Drever-Hall (PDH) locking technique and actively controlling the pumping power. The stabilization setup is shown in Fig. S.8(a) and elaborated in $[59]$. We use two counters with gate time of 1 s to measure the two down-mixed beat frequencies ($f_1$ and $f_2$) at the same time and the recorded frequencies of the two signals allow us to confirm unambiguously that the frequency of the minor comb is offset from the frequency of the major comb by $\Omega_{2/\kappa}$. Fig. S.8(b) shows a small fraction (300 s) of the measured data. One should note that the offset frequency is subtracted from the difference between $f_1$ and $f_2$ in the data presented in Fig. S.8(b). To obtain the Allan deviations of averaging times $< 1$ s, a counter with gate time of 10 $\mu$s is used to measure the frequencies of $f_1$ and $f_2$ sequentially. The detuning locking bandwidth of $\sim 300$ Hz of the PDH locking system and the power control bandwidth of $\sim 0.5$ Hz limited mainly by the response of thermal expansion effect $[60]$ are also shown in the two turning points at averaging times of 0.003 s and 2 s in the Allan deviation plot in the main text.
Figure S.8. Experimental setup for frequency counting and the measured frequency fluctuations. (a) The detailed setup for the stabilization of the microcomb and the measurement of the frequency instabilities of a pair of comb teeth. (b) A fraction of simultaneously measured frequencies of the two beat signals $f_1$ and $f_2$. The modulation frequency $\Omega$ is removed from the frequency difference between $f_1$ and $f_2$, and an arbitrary frequency is subtracted from both $f_1$ and $f_2$ to set the data to around 0 kHz.